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Environmental Considerations of Selected Energy Conserving Manufacturing Process Options: Volume XIII. Phosphoric Acid Industry Report

Arthur D. Little, Inc, Cambridge, Mass.

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Industrial Environmental Research Lab, Cincinnati, Ohio.

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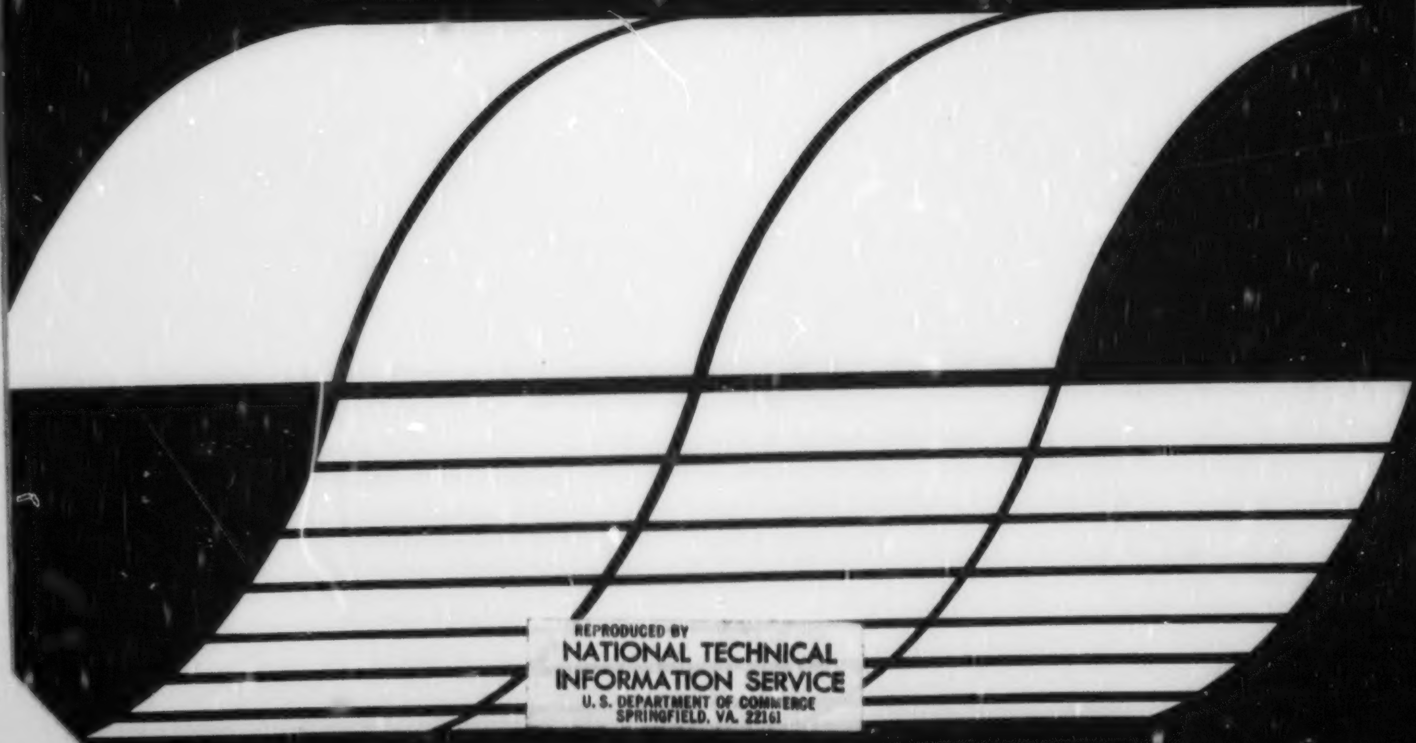
ENVIRONMENTAL CONSIDERATIONS OF SELECTED ENERGY CONSERVING MANUFACTURING PROCESS OPTIONS:

Vol. XIII. Phosphorus/ Phosphoric Acid Industry Report

Interagency
Energy-Environment
Research and Development
Program Report



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16. ABSTRACT

This study assesses the likelihood of new process technology and new practices being introduced by energy intensive industries and explores the environmental impacts of such changes.

Specifically, Vol. XIII deals with the phosphorus and phosphoric acid industry and examines four alternatives: (1) chemical cleanup of wet-process phosphoric acid, (2) solvent extraction process for wet-process phosphoric acid, (3) byproduct sulfuric acid for wet-process phosphoric acid, and (4) "strong acid" system for wet-process phosphoric acid in terms of relative process economics and environmental/energy consequences. Vol. III-XII and Vol. XIV-XV deal with the following industries: iron and steel, petroleum refining, pulp and paper, olefins, ammonia, aluminum, textiles, cement, glass, chlor-alkali, copper, and fertilizers. Vol. I presents the overall summation and identification of research needs and areas of highest overall priority. Vol. II, prepared early in the study, presents and describes the overview of the industries considered and presents the methodology used to select industries.

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ENVIRONMENTAL CONSIDERATIONS OF SELECTED ENERGY CONSERVING MANUFACTURING PROCESS OPTIONS

Volume XIII

ELEMENTAL PHOSPHORUS AND PHOSPHORIC ACID INDUSTRY REPORT

EPA Contract No. 68-03-2198

Project Officer

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This study, consisting of 15 reports, identifies promising industrial processes and practices in 13 energy-intensive industries which, if implemented over the coming 10 to 15 years, could result in more effective utilization of energy resources. The study was carried out to assess the potential environmental/energy impacts of such changes and the adequacy of existing control technology in order to identify potential conflicts with environmental regulations and to alert the Agency to areas where its activities and policies could influence the future choice of alternatives. The results will be used by the EPA's Office of Research and Development to define those areas where existing pollution control technology suffices, where current and anticipated programs adequately address the areas identified by the contractor, and where selected program reorientation seems necessary. Specific data will also be of considerable value to individual researchers as industry background and in decision-making concerning project selection and direction. The Power Technology and Conservation Branch of the Energy Systems-Environmental Control Division should be contacted for additional information on the program.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

EXECUTIVE SUMMARY

PHOSPHORUS/PHOSPHORIC ACID

Phosphate rock is mined in Florida, Tennessee and North Carolina, and in the mountain states of the West. It is converted to commercial end products by digestion with sulfuric acid (the "wet process") or by reduction to elemental phosphorus in an electric furnace. Most of the phosphorus is subsequently converted to phosphoric acid. Although phosphoric acid is the principal commerical product of either method, there is an important difference in the purity of the acid obtained. Furnace acid is essentially a pure chemical that is suitable for detergent, food, and fine chemical uses. Wet-process acid is not pure; it is suitable for fertilizer manufacture but not for most other purposes without cleanup.

The electric furnace process has very high energy requirements, 13,000 kWh as electricity is required per ton of phosphorus produced. This rate is almost as high as that for aluminum and much higher than that of any other significant electroprocessing industry. Wet-process energy requirements are modest, about one-fifth of the electric furnace method on a total energy basis. The total energy requirement of the industry is about 1 x 10^{14} Btu/year; this is a significant requirement.

Pollution problems are related to the impurities in the ore, which for either method must eventually be disposed of as sludge to landfill. Fluorine is an integral part of the ore and its safe containment is vital. Because of the nature of the processes, pollution control is more manageable in the wet process than in the electric furnace method.

More than 80% of the phosphate mined is converted to phosphoric acid by the wet process, and this acid is used for fertilizer materials. A number of proprietary process variations can be expected to compete for new wet process plants, but there are no pollution or energy effects of interest to our study. Uranium has been produced as a wet process system byproduct and interest may be revived. If significant processing for uranium occurs there are pollution problems which must be controlled. Elemental phosphorus once was produced by the blast-furnace process. However, this method requires more total energy, has more severe pollution problems than the electric furnace method, and has poorer economics. Consequently, there is little chance that it will be revived.

Phosphoric acid for detergent manufacture is made from elemental phosphorus; a purity better than that of current wet-process acid is required and furnace acid easily meets these specifications. The detergent market is likely to grow at a rate which will soon outstrip the available supply of phosphorus from the existing electric furnace plants, and cleanup of wet-process acid will be of interest as an alternative to expansion of the electric furnace industry. A chemical method for cleanup has been commercially demonstrated; it appears to be economic and the establishment of several such plants -- each with a capacity of about 50,000 tons of P_2O_5 per year -- is likely in the next 5-10 years. Pollution control would not be much different from that required in the conventional wet-process system. Energy savings over the elemental phosphorus route are substantial.

A solvent extraction system for making clean wet-process acid has been operated commercially outside the United States, but is not well established. It has economic interest under special circumstances and on an energy basis is equivalent to the chemical cleanup option.

The adoption of this system would depend upon the availability of byproduct hydrochloric acid and a satisfactory solution of the environmental problems inherent in the disposal of a calcium chloride brine. In certain locations, for example, where disposal of calcium chloride solutions into underground strata, into large rivers or by ocean dumping might be permitted, the problems of calcium chloride disposal might be less than the problems of disposing of byproduct hydrochloric acid, thereby effecting a more environmentally acceptable solution for a difficult disposal problem.

If the projected expansion in the detergent market is by the wet-process chemical cleanup route six 50,000-ton per-year P_2O_5 plants would be required. At present annual production rates for the entire United States industry (and without consideration of the energy contributions of coke or sulfur) production of 1.4×10^6 tons of P_2O_5 as furnace acid requires 0.09 quads of energy, and 9.0×10^6 tons of P_2O_5 as wet-process acid requires only 0.03 quads. Expansion by 300,000 tons P_2O_5 per year would add 0.019 quads by the electrothermal route but only 0.001 by the wet-process alternate. Net energy saved would be 0.018 quads per year. Moreover, pollution control in these new plants would be attained by established methods that are more easily managed than those necessary at the electric furnace if that industry were expanded.

This report was submitted in partial fulfillment of contract 68-03-2198 by Arthur D. Little, Inc. under sponsorship of the U.S. Environmental Protection Agency. This report covers a period from June 9, 1975 to January 21, 1976.

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During the course of the study we also had occasion to contact many individuals within industry and trade associations. Where appropriate we have made reference to these contacts within the various reports. Frequently, however, because of the study's emphasis on future developments with comparative assessments of new technology, information given to us was of a confidential nature or was supplied to us with the understanding that it was not to be credited. Therefore, we extend a general thanks to all those whose comments were valuable to us for their interest in and contribution to this study.

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ENGLISH-METRIC (SI) CONVERSION FACTORS

To Convert From	To	Multiply By
Acre	Metre^2	4,046
Atmosphere (normal)	Pascal	101,325
Barrel (42 gal)	Metre^3	0.1589
British Thermal Unit	Joule	1,055
Centipoise	Pascal-second	0.001
Degree Fahrenheit	Degree Celsius	$t^\circ_C = (t^\circ_F - 32)/1.8$
Degree Rankine	Degree Kelvin	$t^\circ_K = t^\circ_R/1.8$
Foot	Metre	0.3048
Foot^3/minute	Metre^3/sec	0.0004719
Foot^3	Metre^3	0.02831
Foot^2	Metre^2	0.09290
Foot/sec	Metre/sec	0.3048
Foot^2/hr	Metre^2/sec	0.00002580
Gallon (U.S. liquid)	Metre^3	0.003785
Horsepower (550 ft-lbf/sec)	Watt	745.7
Horsepower (electric)	Watt	746.0
Horsepower (metric)	Watt	735.5
Inch	Metre	0.02540
Kilowatt-hour	Joule	3.60×10^6
Litre	Metre^3	1.000×10^{-3}
Micron	Metre	1.000×10^{-6}
Mil	Metre	0.00002540
Mile (U.S. statute)	Metre	1,609
Poise	Pascal-second	0.1000
Pound force (avdp)	Newton	4.448
Pound mass (avdp)	Kilogram	0.4536
Ton (assay)	Kilogram	0.02916
Ton (long)	Kilogram	1,016
Ton (metric)	Kilogram	1,000
Ton (short)	Kilogram	907.1
Tonne	Kilogram	1,000

Source: American National Standards Institute, "Standard Metric Practice Guide," March 15, 1973. (ANS72101-1973) (ASTM Designation E380-72)

I. INTRODUCTION

A. BACKGROUND

Industry in the United States purchases about 27 quads* annually, approximately 40% of total national energy usage.** This energy is used for chemical processing, raising steam, drying, space cooling and heating, process stream heating, and miscellaneous other purposes.

In many industrial sectors energy consumption can be reduced significantly by better "housekeeping" (i.e., shutting off standby furnaces, better thermostat control, elimination of steam and heat leaks, etc.) and greater emphasis on optimization of energy usage. In addition, however, industry can be expected to introduce new industrial practices or processes either to conserve energy or to take advantage of a more readily available or less costly fuel. Such changes in industrial practices may result in changes in air, water or solid waste discharges. The EPA is interested in identifying the pollution loads of such new energy-conserving industrial practices or processes and in determining where additional research, development, or demonstration is needed to characterize and control the effluent streams.

B. CRITERIA FOR INDUSTRY SELECTION

In the first phase of this study we identified industry sectors that have a potential for change, emphasizing those changes which have an environmental/energy impact.

Industries were eliminated from further consideration within this assignment if the only changes that could be envisioned were:

- energy conservation as a result of better policing or "housekeeping,"
- better waste heat utilization,
- fuel switching in steam raising, or
- power generation.

---

*1 quad = 10^{15} Btu

**Purchased electricity valued at an approximate fossil fuel equivalence of 10,500 Btu/kWh

After discussions with the EPA Project Officer and his advisors, industry sectors were selected for further consideration and ranked using:

- Quantitative criteria based on the gross amount of energy (fossil fuel and electric) purchased by industry sector as found in U.S. Census figures and from information provided from industry sources. The phosphorus/phosphoric acid industry purchased 0.12 quads out of the 12.14 quads purchased in 1971 by the 13 industries selected for study, or 0.4% of the 27 quads purchased by all industry (see Table I-1).

- Qualitative criteria relating to probability and potential for process change, and the energy and effluent consequences of such changes.

In order to allow for as broad a coverage of technologies as possible, we then reviewed the ranking, eliminating some industries in which the process changes to be studied were similar to those in another industry planned for study. We believe the final ranking resulting from these considerations identifies those industry sectors which show the greatest possibility of energy conservation via process change. Further details on this selection process can be found in the Industry Priority Report prepared under this contract (Volume II). On the basis of this ranking method, the phosphorus/phosphoric acid industry appeared in 12th place among the 13 industrial sectors listed.

TABLE I-1

SUMMARY OF 1971 ENERGY PURCHASED IN SELECTED INDUSTRY SECTORS

	Industry Sector	10^{15} Btu/Yr	SIC Code In Which Industry Found
1.	Blast furnaces and steel mills	3.49(1)	3312
2.	Petroleum refining	2.96(2)	2911
3.	Paper and allied products	1.59	26
4.	Olefins	0.984(3)	2818
5.	Ammonia	0.63(4)	287
6.	Aluminum	0.59	3334
7.	Textiles	0.54	22
8.	Cement	0.52	3241
9.	Glass	0.31	3211, 3221, 3229
10.	Alkalies and chlorine	0.24	2812
11.	Phosphorus and phosphoric acid production	0.12(5)	2819
12.	Primary copper	0.081	3331
13.	Fertilizers (excluding ammonia)	0.078	287

(1) Estimate for 1967 reported by FEA Project Independence Blueprint, p. 6-2, USGPO, November 1974.

(2) Includes captive consumption of energy from process byproducts (FEA Project Independence Blueprint)

(3) Olefins only, includes energy of feedstocks: ADL estimates

(4) Amonia feedstock energy included: ADL estimates

(5) ADL estimates

Source: 1972 Census of Manufactures, FEA Project Independence Blueprint, USGPO, November 1974, and ADL estimates.

C. CRITERIA FOR PROCESS SELECTION

In this study we have focused on identifying changes in the primary production processes which have clearly defined pollution consequences. In selecting those to be included in this study, we have considered the needs and limitations of the EPA as discussed more completely in the Industry Priority Report mentioned above. Specifically, energy conservation has been defined broadly to include, in addition to process changes, conservation of energy or energy form (gas, oil, coal) by a process or feedstock change. Natural gas has been considered as having the highest energy form value followed in descending order by oil, electric power, and coal. Thus, a switch from gas to electric power would be considered energy conservation because electric power could be generated from coal, existing in abundant reserves in the United States in comparison to natural gas. Moreover, pollution control methods resulting in energy conservation have been included within the scope of this study. Finally, emphasis has been placed on process changes with near-term rather than long-term potential within the 15-year span of time of this study.

In the phosphorus/phosphoric acid industry, an unusual energy/process option consideration exists. In some phosphate markets, phosphorus produced at the expense of electric energy competes with wet-process phosphoric acid produced by digestion with sulfuric acid, with sulfur serving as both a reagent and an energy source. This consideration turned out to be important to our study.

In addition to excluding from consideration better waste heat utilization, "housekeeping," power generation, and fuel switching, as mentioned above, certain options have been excluded to avoid duplicating work being funded under other contracts and to focus this study more strictly on "process changes." Consequently, the following have also not been considered to be within the scope of work:

- Carbon monoxide boilers (however, unique process vent streams yielding recoverable energy could be mentioned),
- Fuel substitution in fired process heaters;
- Mining and milling, agriculture, and animal husbandry,
- Substitution of scrap (such as reclaimed textiles, iron, aluminum, glass, and paper) for virgin materials.
- Production of synthetic fuels from coal (low-and high-Btu gas, synthetic crude, synthetic fuel oil, etc.); and
- All aspects of industry-related transportation (such as transportation of raw material).

D. SELECTION OF PHOSPHORUS/PHOSPHORIC ACID INDUSTRY PROCESS OPTIONS

Within each industry, the magnitude of energy use was an important criterion in judging where the most significant energy savings might be realized, since reduction in energy use reduces the amount of pollution generated in the energy production step. Guided by this consideration, candidate options for in-depth analysis were identified from the major energy consuming process steps with known or potential environmental problems.

After developing a list of candidate process options, we assessed subjectively

- pollution or environmental consequences of the process change,
- probability or potential for the change, and
- energy conservation consequences of the change.

Even though all of the candidate process options were large energy users, there was wide variation in energy use and estimated pollution loads between options at the top and bottom of the list. A modest process change in a major energy consuming process step could have more dramatic energy consequences than a more technically significant process change in a process step whose energy consumption is rather modest. For the lesser energy-using process steps process options were selected for in-depth analysis only if a high probability for process change and pollution consequences was perceived.

Because of the time and scope limitations for this study, we have not attempted to prepare a comprehensive list of process options or to consider all economic, technological, institutional, legal or other factors affecting implementation of these changes. Instead we have relied on our own background experience, industry contacts, and the guidance of the Project Officer and EPA advisors to choose promising process options (with an emphasis on near-term potential) for study.

Reconciling such difficulties with the desire to cover as wide a spectrum as possible of the consequences of process change, the following candidates were considered:

- Chemical Cleanup of Wet-Process Phosphoric Acid
- Solvent Extraction Process for Wet-Process Phosphoric Acid
- Byproduct Sulfuric Acid for Wet-Process Phosphoric Acid
- "Strong Acid" Systems for Wet-Process Phosphoric Acid
- Blast-Furnace Production of Phosphorus
- Minor Variations of the Conventional Wet-Process Phosphoric Acid System

After discussion with the EPA Project Officer, his advisors, and industry representatives, we chose the first four from this list for analysis because:

- It is not likely that the Blast-Furnace Phosphorus Method will be economically acceptable.
- No pollution or energy considerations of importance are involved in the proprietary process variations offered to the industry by contractors and process licensors.

These last two options are only qualitatively discussed based on readily available information. As it turns out, the byproduct sulfuric acid and the "strong acid" process are also of less interest and are treated with less detail than the "clean-up" processes.

In this study, the phosphorus/phosphoric acid industry description is based on 1973, the latest representative year for the industry for which we had good statistical information. Recognizing that capital investments and energy costs have escalated rapidly in the past few years and have greatly distorted the traditional basis for making cost comparisons, we developed costs representative of the first half of 1975, using constant 1975 dollars for our comparative analysis of new and current processes.

II. FINDINGS AND CONCLUSIONS

A. PRODUCT TRENDS

Phosphorus and its compounds are important requirements for many industries, and the establishment of new plants to support the growth of phosphate products is assured. The principal requirements are in fertilizers, food chemicals, industrial phosphates, and detergents. The fertilizer requirement will continue to be supplied in the conventional manner by digestion of phosphate rock with sulfuric acid in the so-called wet-process route. Elemental phosphorus, food grade chemicals, and industrial phosphates where high purity is required will be derived from elemental phosphorus produced in an electric furnace as at present. Immediate expansion of the electric furnace industry is not foreseen because of the high capital costs required, the shortage and cost escalation of electric power, and the uncertainty of costs for pollution control. As requirements for detergent phosphates increase, the total potential demand for elemental phosphorus will exceed furnace capacity. It is likely that the opportunity for production of detergents from wet-process acid will then be exploited.

B. PHOSPHORIC ACID: ELECTROTHERMAL VS WET PROCESS

Expansion of the production of phosphoric acid for industrial phosphates will require a choice between an elemental phosphorus basis and a wet-process system with the addition of a cleanup method.

From an overall energy standpoint the wet process is much more efficient than the electric furnace process. It requires about 16×10^6 Btu per ton of P_2O_5 product, about one-fifth of the 79×10^6 Btu per ton required for the electrothermal route. The inefficiency of the electrothermal route is, in large measure, due to the use of electricity. About 40×10^6 Btu are lost in fossil fuel-based power generation. Heat losses from the furnace and the reduction of phosphate rock all the way to elemental phosphorus account for the balance of the difference. Both the electric furnace and wet process systems face problems of solids disposal and fluorine disposal, but the problems probably are more severe in the electric furnace process. In addition the electric furnace method must deal with the problem of handling elemental phosphorus.

The wet process requires disposal of about four tons of gypsum per ton of P_2O_5 product. The gypsum disposal problem is manageable in an environmentally satisfactory manner through placement in settling basins for which precautions are taken to prevent leaching into groundwaters of excessive surface runoff. The gypsum wastes contain much of the fluorides which are a component of the phosphate rock and which have been removed from gaseous streams by scrubbing. The removal and management of the fluorides are more easily carried out in the wet process plants. However, the long-term containment of the fluoride-containing gypsum solids is a problem analogous to that facing the steam-electric generating industry in its disposal of sludges from flue gas desulfurization, and it is an area where research and development is needed to delineate the disposal methods most acceptable to regulatory agencies.

In the electric furnace plants, coke must be handled in large quantities and at high temperatures and its control is difficult. In general, the operations of the feed preparation sections and of the electric furnace require extensive solids-handling systems at high temperatures and create rock and carbon dust which is difficult to contain. Problems of quenching hot slag and handling ferrophosphorus (byproduct of electric furnace) also contribute to this dust control problem.

Fluorine is a component of phosphate rock and its disposal is a problem faced by each process. It eventually appears as HF or SiF_4 gas in vent streams from the process and is recovered by scrubbing. These scrubber effluents can be managed more easily in the wet process plants. Finally, the product of the electric furnace is elemental phosphorus and there is an inherent hazard in storing, handling, and shipping this material. Contact with process water is required, and small amounts of entrained phosphorus create problems with cleanup of this "phossy" water.

C. CLEAN WET-PROCESS PHOSPHORIC ACID OPTIONS

There are two methods of modifying the wet-process system so that the phosphoric acid produced is clean enough for production of detergent phosphate: the chemical cleanup and the solvent extraction systems. Economic, energy, and pollution factors significant for these options are summarized in Table II-1.

TABLE II-1

SUMMARY OF COSTS/ENERGY/ENVIRONMENTAL CONSIDERATIONS
OF PROCESS OPTIONS IN PHOSPHORUS/PHOSPHORIC ACID PRODUCTION
Base line process: Electrothermal Phosphoric Acid

	Process Options	
	A	B
	Chemical Cleanup	Solvent Extraction
COSTS	Competitive for detergent-grade phosphates. Less sensitive to escalating electricity, capital costs. Clean wet-process acid = \$294.12/ton P_2O_5. Furnace acid = \$337.82/ton P_2O_5.	Likely to be more expensive than option A. Depends upon cheap HCl
ENERGY	Total energy required is 16×10^6 Btu/ton P_2O_5 instead of 79×10^6 for base line.	Same as A.
ENVIRONMENTAL	Gypsum disposal at 4 tons/ton P_2O_5 is required. Cost = \$15.13/ton P_2O_5 Difficult dust and fume problems at electric furnace avoided. "Phossy" water problem eliminated. Transport of P_4 eliminated. Cost = \$24.11/ton P_2O_5.	Calcium chloride brine at 2.6 tons/ton P_2O_5 must be disposed of, but problem of disposal of HCl is avoided. Same as A.

1. Economics

The economic viability of incorporating one of these methods with a wet-process plant, instead of production from elemental phosphorus, depends to a large extent on the price at which phosphate rock, sulfur, or hydrochloric acid can be made available to the producer. These prices will vary greatly with plant location and among companies; an integration to phosphate rock production is a great asset. We have illustrated this point in Figure II-1 which compares the price at which rock available to an electric furnace producer in the West is competitive with rock prices delivered to a midwestern wet-process plant. A delivered price of suitable rock at $30 per ton to a midwest plant would be competitive with rock at $15 per ton delivered to a western electric furnace plant. At these rock prices the cost of detergent-grade acid from either source would be about $240/ton P_2O_5. These methods of supplying clean wet-process acid have been commercially demonstrated, and the adoption of one or the other for expanded detergent phosphate production is likely.

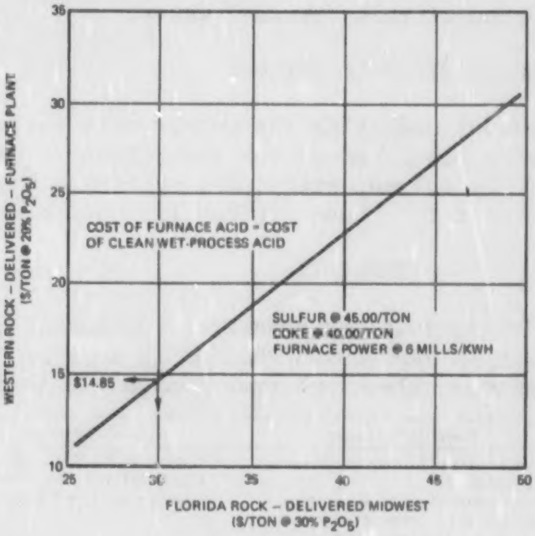

Figure II-1. Phosphate Rock Price Analysis - Midwest Production of Clean Phosphoric Acid

2. Energy

A summary of the energy trade-off associated with these options is tabulated below. The electricity consumed in the furnace is the dominant factor, with the result that furnace acid requires 79 x 10^6 Btu/ton P_2O_5, chemical cleanup 16 x 10^6, and solvent extraction 13 x 10^6. When sulfur is considered as a fuel, its energy contribution is significant (13 x 10^6 Btu) but less than that of the coke charged to the electric furnace. The analogous energy contribution in the solvent extraction system is hydrochloric acid, but we have not attempted to trace its energy content to first sources. It is a byproduct material and its manufacture will not be influenced by use for phosphoric acid.

TOTAL ENERGY REQUIRED (Btu Equivalent)
(10^6 Btu/Ton P_2O_5)

	Furnace Acid	Wet-Process plus Chemical Cleanup	Byproduct HCl and Solvent Extraction
Coke	16	-	-
Fuel	3	-	-
Sulfur	-	13	-
HCl	-	-	No Charge
Steam	-	-	10
Electricity	60	3	3
TOTAL	79	16	13

3. Environmental

a. Effluent Quality

Each of the three* alternate routes to phosphoric acid generate wastewater streams which must be treated prior to discharge. Some of the pollutants present in the treated effluent are common to all three alternatives, while others are characteristic of specific alternatives. In general terms:

- All three alternatives produce treated effluents which contain low (but not insignificant) amounts of soluble phosphates and fluorides.
- The treated effluents from the elemental phosphorus alternative and the chemical cleanup alternative both contain moderately high concentrations of sulfates.
- The treated effluent from the wet process-solvent extraction alternative is generally devoid of sulfates, but contains an extremely large quantity of calcium chloride. The wastewater also contains a moderate amount of n-butanol solvent.

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*Electrothermal phosphoric acid, wet-process plus chemical cleanup, wet-process with solvent extraction.

In our assessment, the high concentration (13.6%) of calcium chloride present in the treated effluent from the wet process-solvent extraction alternative will render it unsuitable for discharge into most receiving streams. For estimation of pollution control costs, we assumed that the most feasible disposal method for this waste stream is deep-well injection (where permitted).

A summary of wastewater flow rates, concentrations, and waste loadings is presented in Table II-2.

We conclude that, from a water pollution standpoint, the wet process-neutralization/precipitation alternative is the most favorable. The wet process-solvent extraction is the least favorable, solely due to the serious calcium chloride brine disposal problem.

b. Wastewater Treatment Cost and Energy Consumption

Economically feasible wastewater treatment control technology is available for each of the three alternatives. Estimates of comparative treatment costs are presented in Table II-3. As shown, the elemental phosphorus alternative is the most expensive, while the wet process (chemical cleanup) alternative is the least costly. The costs are very close to each other; and plant-to-plant variations and site-specific factors could easily upset the relative cost ratios. In general, it can be concluded that no one process has a very significant treatment cost advantage over the other. (It should be noted that deep-well disposal, although perhaps economically feasible, is only a viable option in regions where geological formations are favorable. If the calcium chloride brines were required to be converted to calcium chloride salt, the operation would be energy-intensive. Furthermore, the major markets for calcium chloride are for road deicing, especially in the northern tier of states and Canada, as well as in the cement industry for removal of sodium and potassium as the chloride. In either instance the potential for high concentrations of chlorides entering ground or surface waters has not been decreased from the potential that exists at the plant. In fact, road deicing would result in a much wider potential distribution with probably greater impact on drinking and surface waters. Obviously, the disposal of brines is a significant problem.) The cost of wastewater treatment (as arrived at within the bases of this study) is a relatively small percentage of the total production cost.

None of the wastewater treatment processes is highly energy-intensive, and even the highest wastewater treatment energy consumption is a very small fraction of the total process energy consumption.

TABLE II-2

ALTERNATIVE ROUTES TO PHOSPHORIC ACID-
COMPARISON OF TREATED WASTEWATER CHARACTERISTICS
(Basis: 50,000 tpd P_2O_5)

Wastewater Characteristics	Electrothermal Elemental Phosphorus (mg/1)	(lb/day)	Wet Process Chemical Clean-Up (mg/1)	(lb/day)	Wet Process Solvent Extraction Purification (mg/1)	(lb/day)
Total Suspended Solids	20	145	20	36	20	132
Phosphorus (P_4)	-	-	-	-	-	-
Phosphate (PO_4^{-3})	5	37	20	36	5.4	36
Sulfate (SO_4^{-2})	2020	14,830	2000	3600	-	-
Fluoride (F^-)	15	110	15	27	4.1	27
Calcium Chloride ($CaCl_2$)	-	-	-	-	136,400	901,300
n-Butanol	-	-	-	-	180	1,200
Total Acidity (as $CaCO_3$)	0	0	0	0	no data	no data
Wastewater Flow Rate	0.88 mgd		0.216 mgd		0.792 mgd	

Source: Arthur D. Little, Inc., estimates, based on Development Document for Phosphorus Derived Chemicals . . . U.S. Environmental Protection Agency, EPA 440/1 - 73/006, 1973.

TABLE II-3

ALTERNATIVE ROUTES TO PHOSPHORIC ACID-
COMPARISON OF WASTEWATER TREATMENT COSTS
(Basis: 50,000 tpy P_2O_5)

	Elemental Phosphorus	Wet Process Neutral./Precip. Purification	Wet Process Solvent Extraction Purification
Capital Investment	$930,200	$292,000	$636,000
Direct Operating Costs			
Labor	$ 42,200	$ 48,700	$110,400
Maintenance (Labor & Materials)	37,200	11,700	25,400
Chemicals	147,200	87,800	87,800
Electricity (@ 0.006/kWh)	1,650	13,300	81,000
Sludge Disposal	84,800	161,400	91,000
Total Direct Operating Costs	$313,050	$322,900	$395,600
Indirect Costs			
Depreciation (@ 9%)	$ 83,700	$ 26,300	$ 57,200
Return on Investment (@ 20%)	186,100	58,400	127,200
Taxes and Insurance (@ 2%)	18,700	5,800	12,700
Total Indirect Cost	$288,500	$90,500	$197,100
Annual Total Cost	$601,550	$413,400	$592,700
Unit Cost ($/ton P_2O_5)	$12.03	$8.27	$11.85
Wastewater Treatment Energy Consumption - (Fuel Equivalents - 10^6 Btu/ton P_2O_5)	0.0578	0.140	0.850

Source: Arthur D. Little, Inc., estimates

c. Solid Waste Related to Wastewater Treatment

All three systems process significant amounts of wastewater treatment sludge. In each case, the sludge contains large amounts of calcium fluoride and calcium phosphates and cannot be disposed of indiscriminately. Estimated quantities of wastewater treatment sludge are given below.

Alternative		Quantity of Sludge (tpy wet basis)
I.	Elemental phosphorus	84,750
II.	Wet process - neutralization/ precipitation	80,700
III.	Wet process - solvent extraction	45,500

Although the mass of sludge from the solvent extraction alternative is about one half that of the other alternatives, it is more environmentally objectionable due to the high concentration of soluble chemicals which could rapidly leach from the sludge.

D. USE OF BYPRODUCT SULFURIC ACID

The wet-process industry has the option to operate with purchased byproduct sulfuric acid rather than with sulfur. It is likely that the price of sulfuric acid to such an operation would be negotiated with the result that the cost of phosphoric acid product would be competitive with that from an ordinary wet-process acid system. In addition to purchasing sulfuric acid, a plant independent of a sulfuric acid plant would require steam at about 3 million Btu/ton P_2O_5. This steam might be generated with an on-site steam boiler, or could be purchased from a utility if the plants are adjacent.

Pollution problems directly associated with phosphoric acid would be the same; the pollution problems normally part of the sulfuric acid plant would be eliminated.

E. STRONG ACID PROCESSES

Another alternative system for wet-process phosphoric acid production is to operate the digestion system at phosphoric acid concentrations of about 50% P_2O_5. Evaporation of the product acid is not required under these conditions. The digestion system must be operated at a temperature of about 100°C and the calcium sulfate is separated as the hemihydrate. The process is claimed to be competitive with the standard wet-process system and would be particularly attractive at an integrated fertilizer production site where additional process units can use the steam no longer required for evaporation. Evolution of fluorides from the digestor can be expected to be more severe than with the standard wet-acid system. but the evaporator vent stream is eliminated. On an overall basis, about the same pollution control problems as experienced with the standard wet-process system can be expected.

The adoption of a strong acid process with the use of byproduct sulfuric acid would be attractive on an energy basis.

F. SECONDARY OPTIONS

1. Blast Furnace Phosphorus

Elemental phosphorus can be produced in a blast furnace which utilizes coke as a fuel rather than energy from electricity. There were commercial furnaces of this type, but they were abandoned with the advent of cheap electricity. Capital costs are about 60% higher than for an electric furnace system and the quantity of coke required is more than doubled. The high electric load of the electric furnace is eliminated at the expense of burning fuel in the form of coke. In addition, coke equivalent to that consumed in the electric furnace must be used to achieve the reduction of P_2O_5. Pollution problems associated with dust and furnace ventilation are likely to be more severe than with the electric furnace system because the quantity of furnace gas is greatly increased.

2. Other Options

There are a number of variations of the conventional wet-process system which have only minor interest for our study. We have also reviewed and discussed briefly extraction of uranium from wet-process acid and the exploitation of tailings and low-grade reserves.

Economic, energy, and environmental considerations of use of byproducts H_2SO_4, the "strong-acid" process, and blast-furnace phosphorus are summarized in Table II-4.

TABLE II-4

SUMMARY OF COSTS/ENERGY/ENVIRONMENTAL CONSIDERATIONS OF SECONDARY PROCESS OPTIONS IN PHOSPHORUS/PHOSPHORIC ACID INDUSTRY

	Process Options		
	For mfg of wet-process H_3PO_4 for fertilizer use		For elemental phosphorus
	C Byproduct H_2SO_4	D Strong Acid	E Blast Furnace P_4
Baseline	Wet-Process Phosphoric Acid		Electric Furnace P_4
Process Economics	Investment Reduced Operating costs depend on price of H_2SO_4	Competitive	Probably not Competitive
Energy	Steam required for evaporation. equivalent to 2×10^6 Btu/ton P_2O_5		Electricity eliminated, 130 $\times 10^6$ BTU/ton P_4 saved but equivalent coke must be burned.
Environmental	Sulfuric acid plant pollution; Control costs eliminated	No Change	Utilization of fuel value of CO doubtful - CO must be vented.

III. PHOSPHATE INDUSTRY OVERVIEW

A. INDUSTRY STRUCTURE

Commercial mining of phosphate rock occurs in several areas of the United States. The most important area by far is Central Florida, but major deposits are also being worked in North Carolina, Tennessee, and the Mountain States.

Approximately 83% of the phosphate rock mined (apart from that exported as such) is used in the production of phosphate fertilizers. These are mostly for domestic use, but substantial quantities are exported. The remaining 17% is used in the manufacture of various industrial phosphate materials.

Two processing methods are used to transform phosphate rock into commercial products. The most widely used process produces so-called wet-process phosphoric acid by the acidulation of phosphate rock with sulfuric acid. Phosphoric acid produced by this method is used almost entirely in the production of phosphate fertilizers, although one plant uses this process for industrial phosphates.

The second process consists of the treatment of phosphate rock in an electric furnace to produce elemental phosphorus. Most of this is then used to produce a purer grade of phosphoric acid than that available from the wet-process, although small quantities of phosphorus are used directly in the synthesis of phosphorus-based chemicals. Small quantities of furnace phosphoric acid occasionally find markets in the fertilizer area, but for the most part phosphorus-derived acid is restricted to the industrial phosphate area.

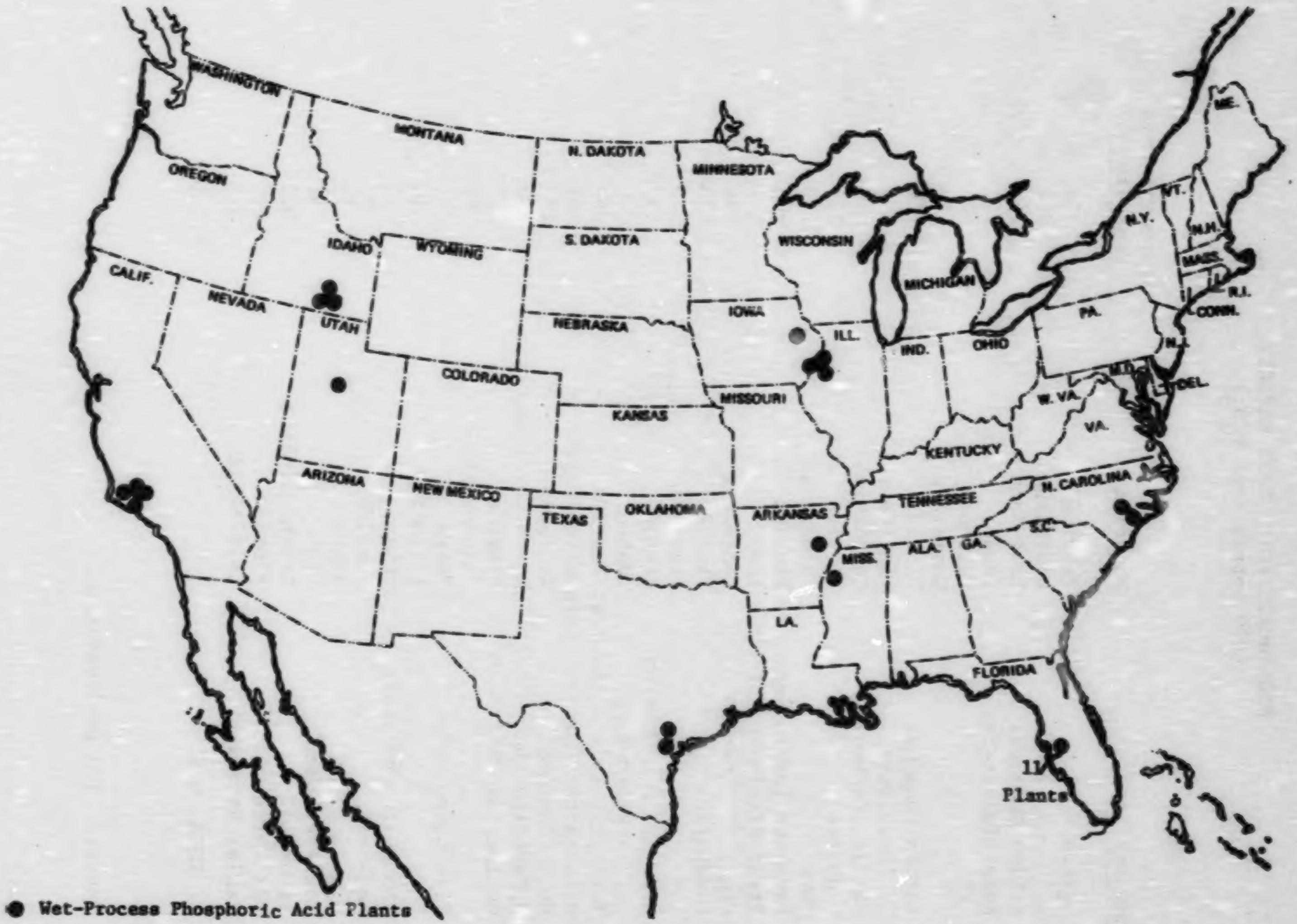
The wet-process phosphoric acid plants are located for the most part adjacent to phosphate rock mines in Florida, North Carolina, and to a small degree in the Mountain States. The production of phosphorus is concentrated in the Tennessee area close to mines, and in the western Mountain States also close to phosphate rock mining activities. There are, however, a number of wet-process phosphoric acid plants located close to fertilizer markets but distant from the phosphate rock mining operations. We have listed wet-process phosphoric acid plants by company and location in Table III-1 and illustrated them in Figure III-1. These include plants currently in operation and those under construction.

TABLE III-1

PHOSPHORIC ACID PLANT CAPACITY
(000 metric tons P_2O_5)

Company	Location	Phosphoric Acid Capacity
Agrico	Florida	306
"	Louisiana	362
Allied Chemical	Louisiana	145
Beker Industries	Idaho	231
"	Illinois	94
"	Louisiana	187
Borden Chemical	Florida	158
CF Industries	Florida	1,136
Collier Carbon	Calfornia	13
Conserve	Florida	136
Duval	California	13
Farmland Industries	Florida	412
First Mississippi Corp.	Iowa	172
Freeport Minerals	Louisiana	680
Gardinier	Florida	493
"	Arkansas	45
W.R. Grace & Company	Florida	297
Gulf Resources	Idaho	29
Int'l.Minerals & Chemical	Florida	680
Mississippi Chemical Corp.	Mississippi	181
Mobil Chemical	Illinois	113
N.Carolina Phosphates	North Carolina	362
Occidental Petroleum	Florida	525
"	California	28
Olin Corporation	Texas	270
"	Illinois	115
Phosphate Chemicals	Texas	45
Royster	Florida	122
Simplot	Idaho	217
Stauffer Chemical	Utah	90
Texasgulf	North Carolina	621
USS Agrichemicals	Florida	240
Valley Nitrogen	California	126
TOTAL U.S.		9,006

Source: TVA publications.


WASHINGTON
OREGON
CALIF.
NEVADA
IDAHO
MONTANA
WYOMING
UTAH
COLORADO
ARIZONA
NEW MEXICO
N. DAKOTA
S. DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
IOWA
MISSOURI
ARKANSAS
LA.
WISCONSIN
ILL.
MICHIGAN
IND.
OHIO
KENTUCKY
TENNESSEE
MISS.
ALA.
GA.
FLORIDA
S.C.
N. CAROLINA
VA.
W. VA.
PA.
N.Y.
MD.
DEL.
N.J.
CONN.
R.I.
MASS.
N.H.
VT.
ME.
11
Plants

● Wet-Process Phosphoric Acid Plants

Source: National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama.

Figure III-1. Wet-Process Phosphoric Acid Plants in the United States

There are some 28 phosphorus furnaces in operation in the United States, operated by six producing companies and the U.S. Government. These are listed in Table III-2.

TABLE III-2

PHOSPHORUS PRODUCERS

Company	Location	Number Operating Furnaces	Operating Furnace Capacity (tons P_4)
Holmes Company	Pierce, Florida	2	20,000
FMC Corporation	Pocatello, Idaho	4	145,000
Mobil Chemical	Nichols, Florida	1	5,000
Monsanto Company	Soda Springs, Idaho	3	110,000
	Columbia, Tennessee	6	135,000
Hooker Chemical	Columbia, Tennessee	3	60,000
Stauffer Chemical	Silver Bow, Montana	2	42,000
	Tarpon Springs, Florida	1	23,000
	Mt. Pleasant, Tennessee	3	45,000
	Muscle Shoals, Alabama	3	40,000
			658,000

Source: National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama.

The production of furnace phosphoric acid from elemental phosphorus is generally located close to market locations because of the economies of shipping concentrated phosphorus instead of the finished acid. There are some 23 furnace phosphoric acid plants in operation in the United States, and these are listed in Table III-3. Figure III-2 shows the geographical locations of the phosphorus furnaces and furnace phosphoric acid plants in the United States.

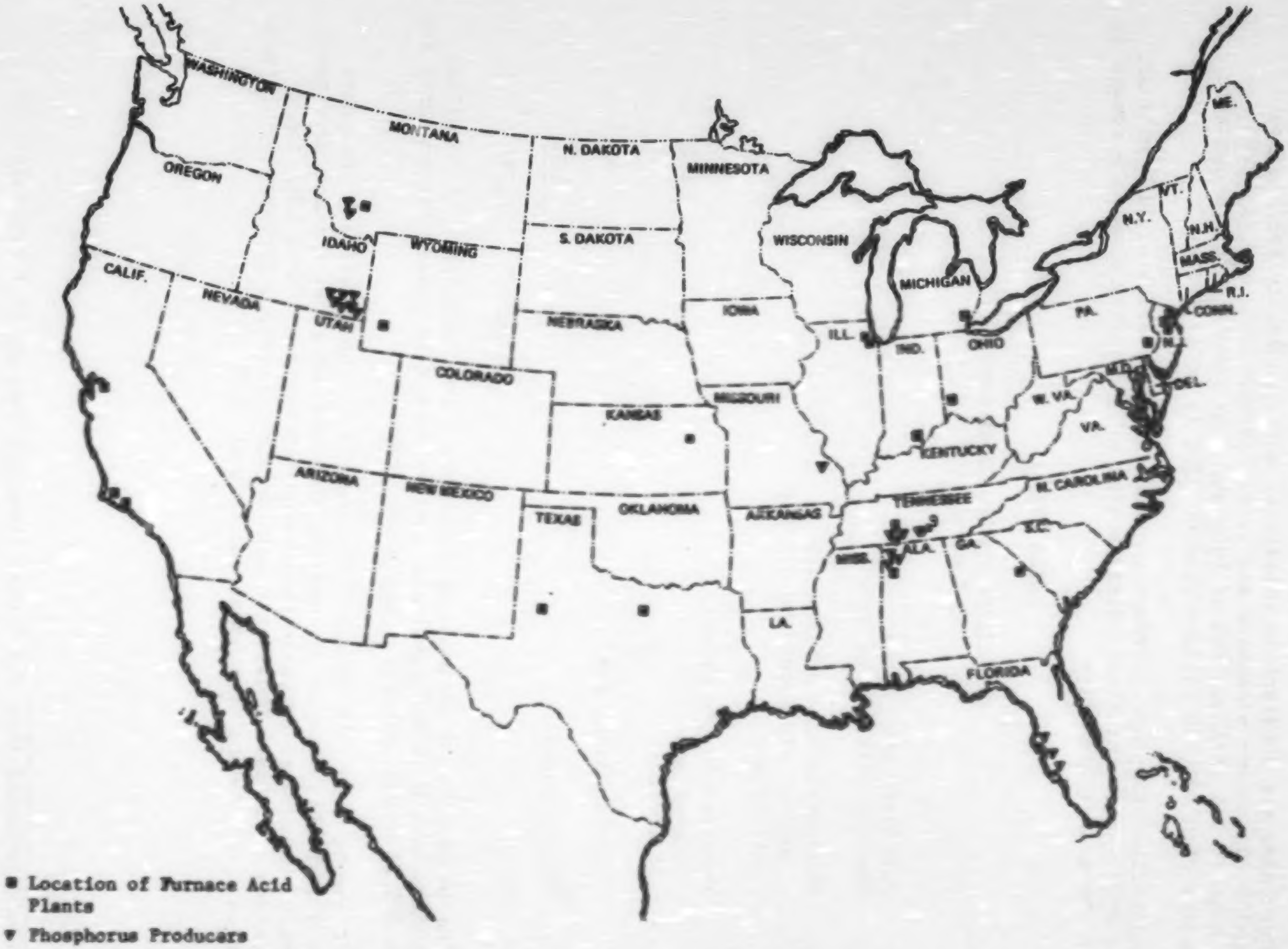
As mentioned above, most wet-process acid is used in the manufacture of various phosphate fertilizers. However there is one plant, operated by the Olin Corporation, Joliet, Illinois, that produces phosphoric acid solely for the production of industrial phosphates. The principal phosphate fertilizers produced from wet-process acid include triple superphosphate, monoammonium phosphate, diammonium phosphate, and various compounds of fertilizers containing all three plant nutrients - nitrogen, phosphate, and potash. Small but significant quantities of phosphoric acid are also used in the production of liquid mixed fertilizers, either solution or suspension.

TABLE III-3

LOCATION OF FURNACE ACID PLANTS

Producers	Plant Location	Grouped Company Capacity (tons P_2O_5)
FMC Corporation	Carteret, New Jersey Lawrence, Kansas Newark, California Green River, Wyoming	340,000
Mobil Oil Corporation	Carteret, New Jersey Fernald, Ohio	115,000
Monsanto Company	Augusta, Georgia Carondolet, Missouri Kearny, New Jersey Long Beach, California Trenton, Michigan	455,000
Occidental Petroleum Corp.	Dallas, Texas Jeffersonville, Indiana Columbia, Tennessee	85,000
Stauffer Chemical Company	Chicago, Illinois Chicago Heights, Illinois Morrisville, Pennsylvania Nashville, Tennessee Richmond, California Silver Bow, Montana South Gate, California	250,000
TVA	Muscle Shoals, Alabama	75,000
Goodpasture, Inc.	Brownfield, Texas	45,000
Total		1,365,000

Source: National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama.


WASHINGTON
MONTANA
N. DAKOTA
MINNESOTA
OREGON
IDAHO
WYOMING
S. DAKOTA
WISCONSIN
MICHIGAN
N.Y.
VT.
N.H.
ME.
MASS.
R.I.
CONN.
CALIF.
NEVADA
UTAH
NEBRASKA
IOWA
ILL.
IND.
OHIO
PA.
N.J.
MD.
DEL.
COLORADO
KANSAS
MISSOURI
W. VA.
VA.
KENTUCKY
ARIZONA
NEW MEXICO
TEXAS
OKLAHOMA
ARKANSAS
TENNESSEE
N. CAROLINA
S.C.
MISS.
ALA.
GA.
LA.
FLORIDA
■ Location of Furnace Acid Plants
▼ Phosphorus Producers

Source: National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama.

Figure III-2. Phosphorus Furnaces and Furnace Phosphoric Acid Plants in the United States

There also are substantial exports of solid phosphate fertilizer, principally diammonium phosphate and triple superphosphate. Exports have run as high as 1.5 million tons of P_2O_5 per year compared to the domestic consumption of about 5.0 million tons of P_2O_5 in fertilizers.

Industrial phosphate consumption amounts to approximately 1.2 million tons of P_2O_5. The approximate distribution of industrial phosphate demand in 1972 is shown in Table III-4.

TABLE III-4

INDUSTRIAL PHOSPHATE DEMAND
(000 tons P_2O_5)

Elemental phosphorus and non-acid derivatives	165
Phosphoric acid derivatives	
Sodium tripolyphosphate (STPP)	600
All others	240
Furnace phosphoric acid	
Direct use	120
Fertilizer	115
Phosphorus exports	45
Miscellaneous	100
TOTAL	1,385

The importance of sodium tripolyphosphate used primarily as a builder in the formulation of detergents is obvious from this table. It accounts for almost 50% of total industrial phosphate demand.

As can be seen from Tables III-2 and III-3, the industrial phosphate industry is highly integrated, most of the manufacture of furnace phosphoric acid being undertaken by basic phosphorus producers.* The production of derivatives of furnace phosphoric acid is also largely undertaken by the same companies that produce phosphorus and furnace acid.

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*It should be noted that the Hooker Chemical Company is a subsidiary of Occidental Petroleum.

B. OUTLOOK FOR THE INDUSTRY

The fertilizer segment of the phosphate industry is currently facing a substantial overcapacity due to a number of new plants that have either come on-stream recently or are expected within the next year or two. This together with a short-term outlook for reduced growth in fertilizer usage should lead to some downward pressure on phosphate fertilizer prices. However, this is sufficiently distinct from the industrial phosphate fertilizer industry that it should have little effect on the latter area.

Much of the future growth in demand for industrial phosphates will depend on the outlook for sodium tripolyphosphate. It is believed that most of the reduction in usage of this compound in detergent formulations because of environmental considerations has already taken place, and future growth in demand for the product would continue at a fairly normal rate - expected to be in the neighborhood of 2%-3% per year. Our market demand forecast thus represents a moderate position. It is about 20% less than if environmental restraints were removed. On this basis, additional plant capacity would probably be needed toward 1980. As discussed elsewhere in this report, this is likely to take the form of new production units, based on clean wet-process phosphoric acid, rather than from the construction of additional phosphorus furnaces.

IV. CURRENT TECHNOLOGY

A. PROCESS CONSIDERATIONS

Phosphate ore is an important mineral resource of the United States; important deposits are located in Florida, Tennessee and North Carolina in the East, and in the western Mountain States. This mineral is a complex of the phosphate and fluoride salts of calcium. It is known as fluorapatite and is commonly represented by the formula $3Ca_3(PO_4)_2 \cdot CaF_2$. Fluorine is usually present in the ore at a ratio of about 10% of the phosphate.

A number of circumstances will probably have important effects upon the development of the technology of the industry. For example, phosphate (P_2O_5) accounts for about 30% of the ore processed; the other 70% includes silica, fluorine compounds, calcium minerals, and a number of metallic constituents. In one way or another this latter group of materials, plus any reagents, such as sulfuric acid or coke, must be disposed of as plant effluents. With the strict standards that must now be considered, the disposal problem has become especially important to the industry. A second important circumstance is the end-use markets for phosphorus and its compounds and the growth of these markets, because the phosphoric acid produced from the wet process must be used primarily in fertilizers, whereas the phosphoric acid that is derived from electric-furnace phosphorus must be used primarily in detergent and phosphate chemical manufacture. Since phosphoric acid is the principal product of each of these processes, one would suppose that there is considerable opportunity to use phosphoric acid from each process interchangeably. Technically, this supposition is correct. Wet-process acid has indeed been used for detergent phosphates and phosphorus from the electric furnace could be converted to phosphoric acid and the acid used in fertilizers. Economically, however, the supposition is false. Purification of the wet-process acid to the degree required for detergent phosphate is difficult and the process has been slow to be adopted commercially. Conversely, the economics of the cleaner electric furnace acid generally have not favored use of this acid in fertilizers.

The importance of this constraint lies in the difference in energy consumption between the wet process and the electric furnace methods. The electric furnace process yields elemental phosphorus (P_4) at an expenditure of about 13,000 kWh/ton of P_4. Coke is also burned as a reductant in the electric furnace and represents an additional major fuel requirement. A considerable part of this energy is released as heat of reaction when the phosphorus is burned to phosphoric acid, but it is not practical to recover it because the elemental phosphorus is not usually converted to phosphoric acid at the electric furnace facility. Instead it is shipped to scattered sites and the acid produced on a much smaller scale. In the wet process, sulfur is shipped to the point of phosphoric acid manufacture, and converted there to the sulfuric acid needed to digest the phosphate rock in efficient plants. Because the sulfur is being converted to sulfuric acid at just one site, the plant can be made efficient enough to recover the heat of combustion from the conversion reaction and use this heat to generate steam for the phosphoric acid plant. The net result is that the heat of combustion of the sulfur is utilized as an important energy input in the wet process for phosphoric acid.

B. BASE LINE: FURNACE ACID-ELECTRIC FURNACE PRODUCTION OF PHOSPHORUS AND CONVERSION OF PHOSPHORUS TO PHOSPHORIC ACID

1. Process Description*

An electric furnace system for the conversion of phosphate rock to elemental phosphorus is shown in Figure IV-1. The primary reaction in the electric furnace is the reduction of P_2O_5 to P_4 by the use of carbon. Elements such as calcium react with silica to form a slag.

Each of the three furnace feed materials--the phosphate ore, the coke, and the silica--must be carefully prepared to allow proper operation of the furnace. The diagram shows one method of preparing a suitable phosphate burden. Phosphate rock is fed to a direct-fired rotary kiln where it is heated to a temperature of incipient fusion (about 2500°F). It is then processed through a screening operation to a suitable size range (1/4 to 1 inch). Oversized material is crushed and recycled to the kiln along with the undersize fraction; the kiln gases must be scrubbed to remove dust and fluorides. Carbon monoxide produced in the electric furnace is used for part of the kiln fuel requirements. The coke and silica streams must also be carefully dried and of a proper size before they are fed to the electric furnace. In addition to being of proper and uniform size, the charge materials must be free from fines in order to feed properly into the electric furnace. The solid furnace burden floats on top of the molten materials in the furnace. The phosphorus is produced in gaseous form as P_4. Carbon monoxide is the principal byproduct and is removed along with the phosphorus. Before condensing the phosphorus it is necessary to operate an electrostatic precipitator on this gas stream to remove and recover dust carried out of the furnace. The phosphorus is then liquified in a water-cooled condenser and the carbon monoxide piped away for use as fuel in the kiln.

There are currently two major sites in the United States for electric furnace phosphorus production. One is in Tennessee where furnaces are operated by Monsanto, Hooker, and Stauffer. The TVA also operates a large furnace system there, but has announced that is will be shut down. In the Mountain States, Monsanto and FMC operate furnaces in Idaho and Stauffer

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*(Waggaman et al, 1952), (Van Wazer, Jr., 1961)

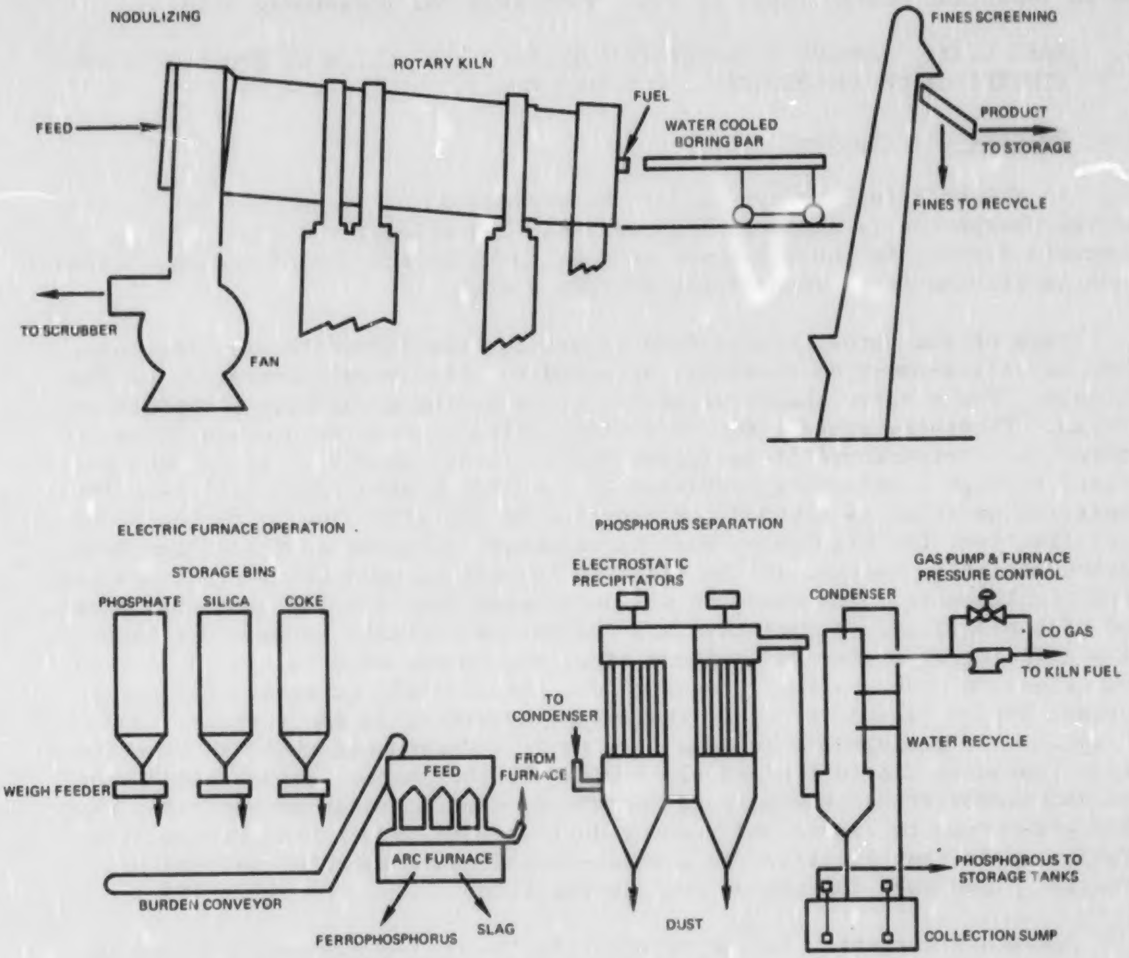
NODULIZING
ROTARY KILN
FEED
FUEL
WATER COOLED
BORING BAR
FINES SCREENING
PRODUCT
TO STORAGE
FINES TO RECYCLE
TO SCRUBBER
FAN
ELECTRIC FURNACE OPERATION
STORAGE BINS
PHOSPHATE
SILICA
COKE
WEIGH FEEDER
FEED
ARC FURNACE
BURDEN CONVEYOR
FERROPHOSPHORUS
SLAG
PHOSPHORUS SEPARATION
ELECTROSTATIC
PRECIPITATORS
TO
CONDENSER
FROM
FURNACE
DUST
CONDENSER
GAS PUMP & FURNACE
PRESSURE CONTROL
CO GAS
TO KILN FUEL
WATER RECYCLE
PHOSPHOROUS TO
STORAGE TANKS
COLLECTION SUMP

Figure IV-1. Elemental Phosphorus Production

operates one in Montana. There is little important use of elemental phosphorus by itself. The majority of it is converted by burning in air and absorption of the oxide in water to make pure phosphoric acid suitable for detergent, food grade, and fine chemical end-uses. There is some production of phosphoric acid in this manner at the site of phosphorus production, but the practice generally is to ship the phosphorus to the point of end-use and run a smaller phosphoric acid plant at that site. It is believed that most phosphorus burning plants operate at a rate of 50,000 tons of P_2O_5, or less, annually.

2. Effluents

There are severe pollution control problems associated with elemental phosphorus production. Principal effluents and their source are indicated in Figure IV-2.

a. Water Pollution

There are three major wastewater streams generated by the electric furnace production of elemental phosphorus:

- Nodulizer scrubber water blowdown - Gaseous emissions from the phosphate rock nodulizer are dusty and contain fluorides (such as HF or SiF_4); therefore, they must be controlled by means of a wet scrubber. The scrubber water is recycled. The necessary purge stream from the recycle system is acidic, contains phosphates, sulfates, fluorides, and suspended solids, and must be treated prior to discharge.
- Slag quench water - Furnace slag is cooled by means of quenching with a water stream. The slag quench water is slightly alkaline, contains phosphates, sulfates, fluorides, and suspended solids, and also must be treated prior to discharge.
- "Phossy" water - A notoriously difficult stream is the so-called "phossy" water. This stream results from the necessary contact of liquid phosphorus with water in the condenser and in the transfer lines for phosphorus. Water is also used as a seal in storage and transport to prevent exposure of the phosphorus to air. The result is that water discharged from these operations contains a small amount of very finely divided phosphorus in suspension. The "phossy" water also contains significant amounts of phosphates and fluorides.

The volume and pollutional loadings of the various wastewater streams can vary considerably from plant to plant, depending on process configuration and other site specific conditions. In some plants there is a high degree of wastewater recycle; in other plants there is none. In any event, wastewater discharged from elemental phosphorus plants will have to be treated to remove phosphorus, phosphates, and fluorides, and to neutralize acidity.

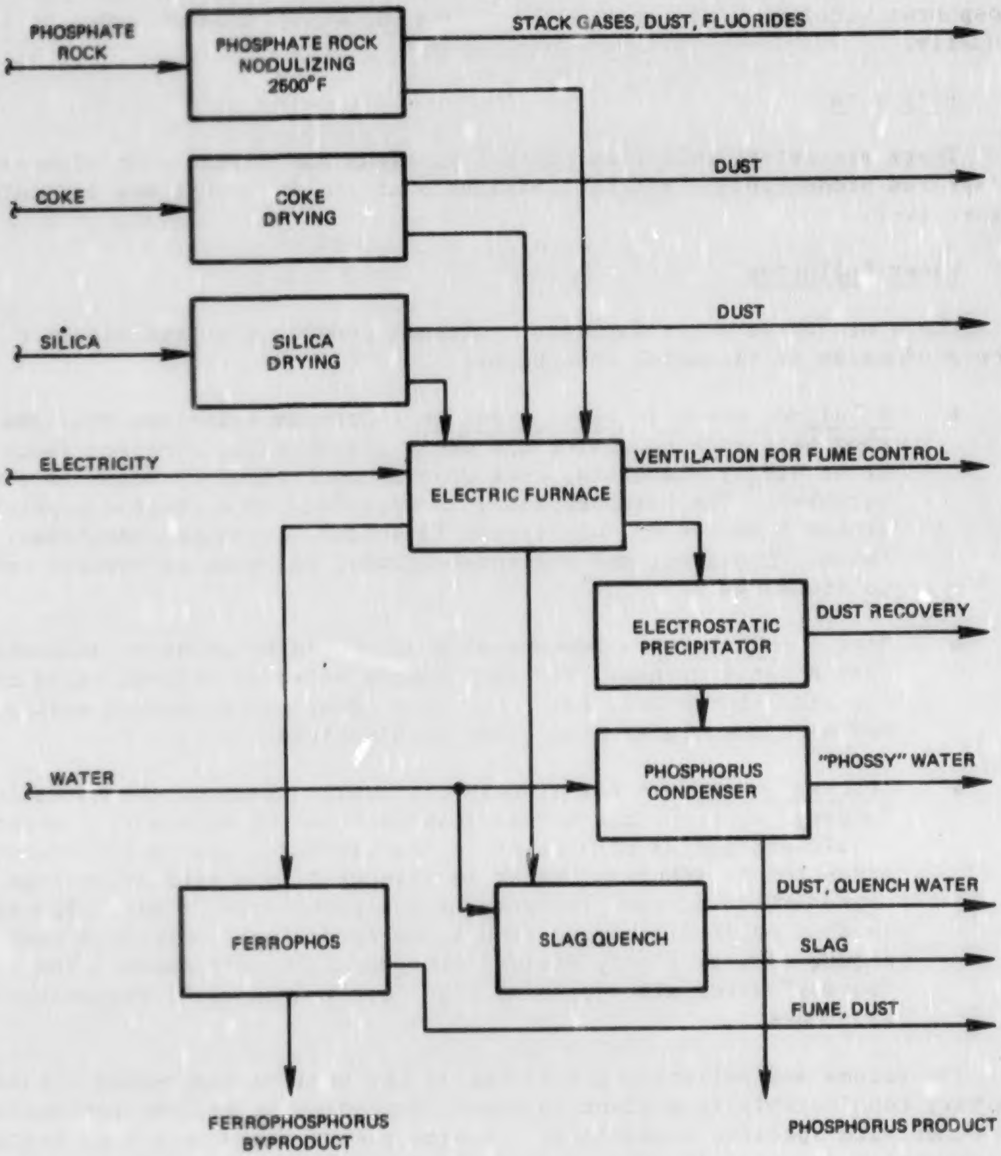
PHOSPHATE ROCK
PHOSPHATE ROCK NODULIZING 2500°F
STACK GASES, DUST, FLUORIDES
COKE
COKE DRYING
DUST
SILICA
SILICA DRYING
DUST
ELECTRICITY
ELECTRIC FURNACE
VENTILATION FOR FUME CONTROL
ELECTROSTATIC PRECIPITATOR
DUST RECOVERY
WATER
PHOSPHORUS CONDENSER
"PHOSSY" WATER
FERROPHOS
SLAG QUENCH
DUST, QUENCH WATER
SLAG
FUME, DUST
FERROPHOSPHORUS BYPRODUCT
PHOSPHORUS PRODUCT

Figure IV-2. Process Effluents - Electric Furnace Phosphorus

Metallic elements, originating in phosphate rock, can be present in the wastewater. A typical analysis is presented below:

MINOR CONSTITUENT ANALYSIS
ELECTRIC FURNACE PHOSPHORUS OPERATION*
(%)

Constituent	P	Si	Ca	Fe	Al	Cr	V	Ni	Mn
Slag	0.5	18	34	0.1	3.1				
Ferrophosphorus	27	0.15		59		4.5	5.4	0.7	0.5

Water pollution regulatory constraints imposed upon the phosphorus industry are mainly the results of the applicable effluent limitations guidelines published by the Environmental Protection Agency (Effluent Guidelines, 1974). The effluent limitations guidelines are based on a technical study commonly referred to as the EPA Development Document (Development Document... Phosphorus-Derived Chemicals, 1973). The function of the Development Document is to characterize the industry, describe the sources of water pollution, the wastewater characteristics, control technology currently in use, suggested permissible effluent levels, recommended technology for their attainment, and cost estimates for the implementation of such technology. For this study, much of the data on wastewater characteristics and type of treatment technology required have been taken from the Development Document. However, the industry has taken exception, through legal action, to the use of these data by the EPA in developing effluent limitation guidelines. These objections apply especially to the industry-wide application of data which, it contends, are both site and time specific. Without attempting to make a judgment on the validity of these claims, we have chosen to utilize the data as it was reported rather than attempt an independent modification which would be apt to create additional confusion.

Characteristics of the various raw wastewater streams generated from an elemental phosphorus plant of the size used in this study are presented in Table IV-1.

There are a number of treatment alternatives that are currently being employed or are potentially applicable. The most general treatment method is as follows:

1. Combine the nodulizer scrubber liquor blowdown with the slag quench water and treat with lime (in a clarifier or settling pond) to precipitate fluorides and phosphates as calcium salts. In addition, the lime treatment removes suspended solids and neutralizes acidity.

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*(Van Wazer, Jr., 1961)

TABLE IV-1

CHARACTERISTICS OF RAW PROCESS WASTEWATER FROM PHOSPHORUS MANUFACTURE

Basis: 100,000 tpy phosphorus production (230,000 tpy as P_2O_5)

Wastewater Characteristic	Combined Raw Wastewater		Total Treated Effluent	
	(mg/l)	(lb/day)	(mg/l)	(lb/day)
Total Suspended Solids	525	17,550	20	670
Phosphorus (P_4)	-	-	-	-
Phosphate (PO_4^{-3})	56	1,880	5	167
Sulfate (SO_4^{-2})	2,020	67,390	2,020	67,390
Fluoride (F^-)	480	16,010	15	500
Total Acidity (as $CaCO_3$)	990	33,040	0	0
Wastewater Flow Rate	4.0 mgd		4.0 mgd	

Source: Arthur D. Little, Inc., estimates, based on " . . . Development Document for Phosphorus Derived Chemicals . . .", EPA.

2. Treat the phossy water with lime or other coagulants to remove colloidal phosphorus and to precipitate soluble fluoride and phosphates. The entire phossy water stream is then recycled back to the process. The result is that there is zero discharge of phossy water.

Based on the characteristic wastewater flow rates, pollutional loadings and characteristic removal efficiencies, an estimate of the treated wastewater composition is presented in Table IV-2.

The plant for conversion of phosphorus to phosphoric acid must include a scrubbing system to remove acid fumes from the furnace effluent, but this is a conventional unit and adequate control is not difficult or expensive.

The treatment system required to achieve the effluent levels (shown in Table IV-2) consists of:

1. Combined nodulizer scrubber liquor and slag quench water effluent treatment -
   - clarifiers (2 units),
   - chemical feed system,
   - sludge thickener,

TABLE IV-2

ELECTRIC FURNACE PRODUCTION OF PHOSPHORIC ACID WASTEWATER CHARACTERISTICS

Basis: 100,000 tpy production (as P_4)
330 operating days/year

Wastewater Characteristic	Nodulizer Scrubber Liquor*		Phosphorus Condenser Plus Other Phossy Water		Slag Quenching Water		Combined Wastewater	
	(mg/l)	(lb/day)	(mg/l)	(lb/day)	(mg/l)	(lb/day)	(mg/l)	(lb/day)
Total Suspended Solids	280	5,100	135	8,190	820	12,450	273	25,740
Phosphorus (P_4)	-	-	90	5,460	-	-	58	5,460
Phosphate (PO_4)	70	1,270	220	13,350	40	610	162	15,230
Sulfate (SO_4)	1,200	21,830	-	-	3,000	45,560	717	67,390
Fluoride (F^-)	730	13,280	270	16,380	180	2,730	344	32,390
Total Acidity (as $CaCO_3$)	2,000	36,380	-	-	-	-	351	33,040
Total Alkalinity (as $CaCO_3$)	-	-	-	-	220	3,340	-	-
Wastewater Flow Rate	2.18 mgd		7.27 mgd		1.82 mgd		11.27 mgd	

*Assumes scrubber liquor is recirculated with a 10% blowdown.

Source: "...Development Document for the Phosphorus Derived Chemicals..." U.S. Environmental Protection Agency, EPA 440/1-73/006, 1973.

- vacuum filtration (for sludge dewatering),
- all necessary pumps, piping, and auxiliary equipment.

2. Phossy water treatment and recycle -
    - clarifiers (2 units),
    - chemical feed system,
    - sludge thickener,
    - vacuum filtration (for sludge dewatering),
    - all necessary pumps, recycle piping, and auxiliary equipment.

Capital and operating cost estimates along with the quantities of chemicals, energy, and sludge associated with the treatment system are presented in Table IV-3.

It should be noted that the costs presented in Table IV-3 are for the specific size plant used in this study and have been developed mainly for comparative purposes; they in no way are intended to represent industry-wide treatment costs. The estimate is for a consolidated P_4/H_3PO_4 plant, such as those in the west.

TABLE IV-3

ELECTRIC FURNACE PRODUCTION OF PHOSPHORUS AND PHOSPHORIC ACID WASTEWATER TREATMENT COSTS

Basis: 100,000 tpy phosphorus production (230,000 tpy as P_2O_5)

	TOTAL PLANT
CAPITAL INVESTMENT	$4,279,000
DIRECT OPERATING COST	
Labor	194,000
Maintenance (Labor and Materials)	171,000
Chemicals	677,000
Electricity (@ $0.006/kWh)	7,600
Sludge Disposal	390,000
TOTAL DIRECT OPERATING COST	$1,439,600
INDIRECT COSTS	
Depreciation (@ 9%)	385,000
Return on Investment (@ 20%)	856,000
Taxes and Insurance (@ 2%)	86,000
TOTAL INDIRECT COST	$1,327,000
TOTAL ANNUAL COST	$2,766,600
UNIT COST: ($/ton as P_4)	$ 27.67
($/ton as P_2O_5)	$ 12.03

Notes:

1. Treatment consists of:
   a) Lime treatment and clarification of combined nodulizer scrubber liquor blowdown and slag quench water;
   b) Lime treatment and clarification of phossy water, with total recycle of treated phossy water stream.
2. Capital investment adjusted to March 1975 level (ENR=2126).

Source: Arthur D. Little, Inc. estimates.

Even though the treatment described is capable of producing a liquid effluent of relatively low fluoride and phosphate content, there is still a serious solid-waste disposal problem. Since furnace slag is usually sold to contractors, the major source of solid waste destined for ultimate disposal is wastewater treatment sludge. The sludge volume is large (84,750 tpy @ 30% solids) and contains very high concentrations of calcium fluoride, calcium-phosphate salts, sulfates, and elemental phosphorus.

b. Solids Disposal

The land disposal of sludges from phosphorus manufacture requires considerable acreage with the concomitant problems of surface runoff and seepage into groundwaters. Because slight variations in process operating conditions for all wet chemistry methods can cause wide variations in the nature of the sludges, e.g., these may vary from high-solid content cakes to slurries, the magnitude of the solids waste disposal problem can also vary widely. In addition, elemental phosphorus and arsenic compounds can result in low-level occurence of volatile species, such as the phosphorus oxides and arsine. The latter is known to occur from natural sources as part of the environment's arsenic cycle; however, local concentrations of these substances, which may be of concern in certain disposal areas, are usually the results of leaching from solids disposal. The prevention of groundwater seepage and the control of surface runoff by a variety of methods - such as lining of disposal areas, maintenance of water cover during operational periods and perhaps, ultimately, covering of disposal areas - will probably require increasing attention. Because the costs of these controls are highly site-specific, we have made no attempt to detail probable costs.

c. Air Pollution

Air pollution control is a significant problem in the phosphorus plant. The process importance of handling dusty streams in the phosphorus plant is illustrated by the need to remove dust generated from processing raw materials (phosphate rock, coke, and silica) at a rate more than 10 times that of the product. These particulates are produced particularly in the high-temperature rotating equipment, but also escape from conveyors, etc. They are usually finely divided and contain carbon and fluorides. However, removal of particulates can be carried out in conventional air pollution control equipment such as cyclones, fabric filters, or electrostatic precipitators.

Although dry air pollution control systems are widely used, one air stream that requires scrubbing is the emission from the phosphate nodulizer because it contains fluorides, such as HF or SiF_4. As mentioned earlier, this wastewater stream is combined with other wastewater streams for treatment in a common facility. Similarly, the plant for conversion of phosphorus to phosphoric acid must utilize water scrubbing to remove acid fumes from the effluent and, again, the wastewater stream is recycled to process or combined with others for treatment.

Air pollution control systems of the type described are normal features of present plants. Because the capital investments associated with air pollution control systems are intimately involved with the manufacturing process and, consequently, are highly dependent upon specific site conditions, it was felt that estimates would have little meaning for comparative purposes. Although their costs are not separately estimated, they are included in the capital and operating costs presented for the electric furnace system.

3. Energy Requirements

Electric furnace production of phosphorus is a very energy-intensive operation. As illustrated in Table IV-4, it consumes 13,000 kWh/ton of phosphorus, a rate second only to aluminum among the selected electric furnace-based commercial operations included in the scope of this study. The process is inherently wasteful because phosphorus itself is not the major commercial product; in the subsequent combustion operation the heat released upon oxidizing the phosphorus to P_2O_5 is lost to the atmosphere and to cooling water.

TABLE IV-4

IMPORTANT ELECTROCHEMICAL OPERATIONS

Process	Electricity Required kWh/ton product
Aluminum	15,600
Phosphorus	13,000
Ferro-manganese (75%)	4,600
Zinc	3,000
Calcium carbide	2,800
Copper (electrowinning)	2,400

Coke charged to the furnace is a significant fuel requirement, but is burned only to carbon monoxide; it must be recovered and piped to the burden preparation unit for full use of its fuel value. Energy requirements as auxiliary fuel for the nodulizer and as electricity for pumping operations amount to about 10% of the electricity requirement of the electric furnace itself.

TOTAL EQUIVALENT ENERGY - SUMMARY

As Electricity	13,000 kWh =	137×10^6 Btu/ton P_4 =	60×10^6 Btu/ton P_2O_5
As Coke	1.9 tons C =	36×10^6 Btu/ton P_4 =	16×10^6 Btu/ton P_2O_5
As Supplementary Fuel		6×10^6 Btu/ton P_4 =	3×10^6 Btu/ton P_2O_5
		179×10^6 Btu/ton P_4 =	79×10^6 Btu/ton P_2O_5

4. Economic Factors

The costs of conversion of phosphate rock to elemental phosphorus by the electrothermal reduction process are detailed in Table IV-5. This estimate is based on 1975 construction costs of a new plant in the Mountain States to produce phosphorus at a rate of 100,000 tpy. A more realistic event would probably be the expansion of one of the existing three plants in the region by the addition of a furnace at about half that capacity. However, we have no way of estimating the cost of such incremental production on a realistic basis. Because of economies of scale in the larger plant, the unit cost of P_4, as estimated, is probably not far from that of incremental production in an expanded plant. The result is that a producer considering expansion of his phosphorus business by the electrothermal route must look at a production cost of about $540/ton of phosphorus. Raw materials account for a major fraction of this cost at $290/ton. Phosphate rock and coke are the major raw materials and since the 1973 "energy crisis," prices have been volatile. The prices ($20/ and $40/ton respectively) represent our best judgment of current values, but may be quite different from an actual local circumstance. Phosphate rock costs are, to a certain extent, fuel-dependent, but as captive operations of the phosphorus producer can be kept under better cost control than coke or electricity.

Electricity is the major energy cost and amounts to $78/ton of phosphorus. The current price of electricity is 6 mils/kWh and its future is quite uncertain. It is likely that the price of power in the West will increase by a factor of 50-100% in the next decade. The price of electricity for electric furnace phosphorus use is negotiated and subject to contract with the power company. The high base load at a good power factor commands a favorable price.

A large labor force is required for operation of an elemental phosphorus plant. About 220 men are employed in the direct operating staff, and more than 100 additional people in the maintenance force. The result is a total labor cost (including labor overhead) of about $75/ton of phosphorus. Fixed costs for plant overhead, taxes, insurance, and depreciation bring the total estimated cost to $543.31. The depreciation cost is $28.80 and is based on an 11-year depreciation of the plant.

TABLE IV-5

ESTIMATED COST OF ELEMENTAL PHOSPHORUS MANUFACTURE

Product: Elemental Phosphorus
Process: Electrothermal Reduction
Location: Western States

Annual/Design Capacity: 100,000 tons P_4
Fixed Investment: $64,000,000

Annual Production: 100,000 tons P_4

	Units Used in Costing or Annual Cost Basis	$/unit	Units/ton P_4	$/ton P_4
Variable Costs				
Raw Materials				
Phosphate rock	tons	20.00	10.0	200.00
Silica	tons	1.40	1.25	1.75
Coke	tons	40.00	1.9	76.00
Electrodes	lbs	0.24	53.0	12.72
				290.47
Energy				
Electricity	kWh	0.006	13,000	78.00
Fuel	10^6 Btu	0.80	11.0	8.80
				86.80
Water				2.00
Labor				
Direct operating labor	Man-hrs	6.00	5.15	30.90
Direct supervisory wages	15% Op. Lbr			4.64
Maintenance labor	Man-hrs	6.50	3.0	19.50
Maintenance supervision	15% Mnt. Lbr			2.93
Maintenance material	3% of CI			20.00
Labor overhead	30% of Wages			17.39
Operating Supplies				5.00
Ferrophosphorus credit	tons	47.00	0.14	<6.58>
Slag credit	tons	0.85	7.2	<6.12>
Total variable cost				466.93
Fixed Costs				
Plant overhead	60% of Wages			34.78
Local taxes & ins.	2% CI			12.80
Depreciation	9% CI			28.80
Total cost of manufacture				543.31
20% return on investment (pre-tax)				128.00
Pollution control (Table IV-3)				27.67
				698.98

Source: Arthur D. Little, Inc. estimates

An additional economic factor in the phosphorus business is the depletion credit. This credit should not be considered a part of the usual cost structure because it depends on profit. If there is no profit, there is no depletion credit allowed. It is really a credit against income tax; the depletion is applied as a reduction of profit before tax is calculated. Its actual calculation follows a complex formula that depends upon the transfer of the elements of the cost of mining and beneficiation of the phosphate rock as part of the total cost of the operation of a phosphorus furnace plant.

In Table IV-6 we have estimated the cost of manufacture of phosphoric acid from elemental phosphorus. This estimate is based upon a plant in the midwest with an annual capacity of 50,000 tpy of P_2O_5. Capital investment for such a facility as of 1975 would be $1,700,000. Phosphorus delivered to midwest locations would cost about $570/ton. At a conversion efficiency of 0.44 ton of phosphorus/ton of P_2O_5, the phosphorus represents $250/ton cost to phosphoric acid. Conversion costs amount to about $12/ton for a total cost at the plant site of $262.67/ton of P_2O_5.

C. BASE LINE - WET-PROCESS PRODUCTION OF PHOSPHORIC ACID

1. Process Description*

Figure IV-3 is a block flow diagram which shows the method for converting phosphate rock to phosphoric acid by digestion with sulfuric acid. The sulfuric acid is manufactured from sulfur. The primary product of the digestion and filtration section is 32% phosphoric acid which is concentrated by evaporation to the 54% P_2O_5 product.

On an overall basis, sulfuric acid reacts with tricalcium phosphate to precipitate gypsum and form phosphoric acid in solution:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_{4(sol)}.$$

Conditions in the digestion system must be carefully controlled to disperse and dissolve all of the phosphate rock, and to precipitate gypsum without co-precipitation of unreacted rock and in the form in which it can be readily filtered and washed. The system is arranged so that phosphate rock can first react with a recycled stream of phosphoric acid forming

$$Ca_3(PO_4)_2 + 4H_3PO_4 \rightarrow 3Ca(H_2PO_4)_2$$

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*(Waggaman, 1952; Van Wazer, Jr., 1961)

TABLE IV-6

ESTIMATED COST OF PHOSPHORIC ACID MANUFACTURE

Product: Phosphoric Acid

Process: via Elemental Phosphorus

Location: Midwest

Fixed Investment: $1,700,000

Annual/Design Capacity: 50,000 tons P_2O_5

Annual Production: 50,000 tons P_2O_5

	Units	$/unit	Units/ton P_2O_5	$/ton P_2O_5
Variable Costs				
Phosphorus	tons	570.00	0.44	250.80
Energy				1.00
Water				1.00
Labor				3.50
Maintenance				1.50
Labor Overhead				1.00
Total Variable Costs				258.87
Fixed Costs				
Plant Overhead				2.00
Local taxes & ins.	2% of CI			0.34
Depreciation	9% of CI			1.53
Total				262.67
20% Return on investment (pretax)				
Phosphorus plant				56.32
Phosphoric acid plant				6.80
Pollution control				12.03
				337.82

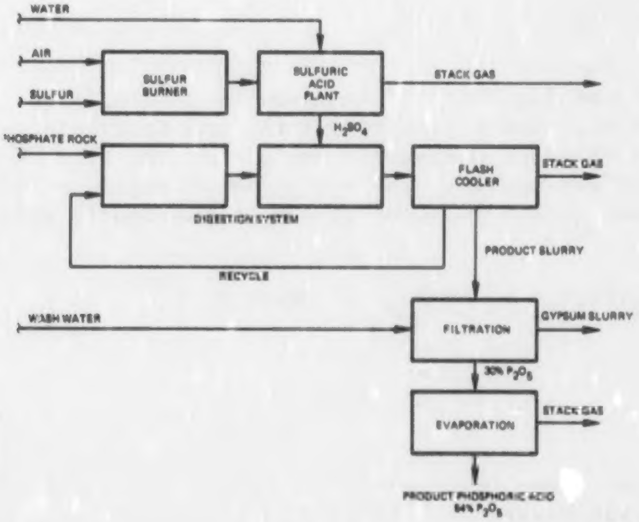

WATER
AIR
SULFUR
SULFUR BURNER
SULFURIC ACID PLANT
STACK GAS
H_2SO_4
PHOSPHATE ROCK
FLASH COOLER
STACK GAS
DIGESTION SYSTEM
PRODUCT SLURRY
RECYCLE
WASH WATER
FILTRATION
GYPSUM SLURRY
30% P_2O_5
EVAPORATION
STACK GAS
PRODUCT PHOSPHORIC ACID
54% P_2O_5

Figure IV-3. Phosphoric Acid - Wet Process

monocalcium phosphate in solution. In a subsequent digestion tank, the sulfuric acid is then mixed at a controlled rate with the slurry:

$$3Ca(H_2PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 \downarrow + 6H_3PO_4.$$

The temperature, strength of the phosphoric solution, and degree of free sulfuric acid present are controlled at conditions to give the optimum digestion efficiency, and the best form of gypsum for filtration. Total residence time in the digestion system is about 6 hours. The reaction is strongly exothermic and cooling is required to maintain the desired temperature. Cooling is accomplished in some plants by sparging with air and evaporation in the digesters. Another common system is to pump the recycled slurry through a flash cooler. The recirculation rate is high enough so that the temperature rise through the digestion system is not excessive before cooling is accomplished in the flash cooler. Impurities in the phosphate rock include silica, fluorine, iron, aluminum, sulfate, and minor constituents such as magnesium, sodium, potassium, manganese, copper, zinc, lead, titanium, chromium, molybdenum, nickel, arsenic, vanadium, and uranium. Carbon in the form of organic matter is particularly troublesome because it promotes foam in the digestion system. This foam can often be controlled by adding anti-foam agents, but with some rocks calcination to burn off the organic matter is necessary before it can be used in wet process systems.

The slurry from the digestion system is processed on a rotary vacuum filter to separate the gypsum for disposal. It is necessary to wash gypsum cake carefully to get full recovery of phosphate, and the washing conditions must be carefully controlled to prevent blinding of the filter medium. All of the washwater used appears as water of dilution, and the product acid and the water balance must be carefully managed from this standpoint.

Acid from the filter has a phosphoric acid concentration of about 30-32% P_2O_5. This material is next concentrated to 54% P_2O_5 in an evaporation system. The crude acid is always saturated in calcium sulfate and precipitation upon concentration is a major problem. A recirculation system is used to help minimize scaling of the evaporator surface.

2. Effluents

a. Water Pollution

The major waste stream from the phosphoric acid plant is the gypsum slurry from the filtration step. The gypsum cake is slurried in recirculated water and pumped to a settling basin. The phosphoric acid plants are usually located close to the phosphate mines and it is not difficult to form a satisfactory settling pond in a mined out area. A substantial fraction of the fluorine originally present in the phosphate rock is discharged along with the gypsum as sodium silico fluoride. This stream also contains free phosphoric acid and is slightly acidic.

Although there is no inherent wastewater stream from the sulfuric acid plant, tube leaks in the cooling system can result in intermittent discharges of sulfuric acid.

The characteristics of the gypsum pond water have been reported in the Development Document (Development Document...Basic Fertilizer Chemicals, 1974) for Effluent Limitation Guidelines. The Document also provides data on the type of treatment required and the anticipated treated effluent characteristics.

The main pollutants of concern present in the gypsum pond water are soluble phosphates and fluoride, both of which may be typically present in the 8,000 to 15,000 mg/l concentration range. As long as this water is contained within the pond, there is no water pollution problem. At some plants rainfall during the dry season is low enough to approach this condition for many consecutive days. Zero discharge has been proposed as an ultimate standard, but its practice by solar evaporation at any location and the cost of forced evaporation are currently part of the litigation now in the courts. For this report we are interested in a midwest location where rainfall is normally in the 30 to 40 in/yr range. Our pollution control estimates are therefore based on treatment of overflow from the pond after settling and containment of the gypsum and other settleable solids. Due to the high phosphate and fluoride concentrations in the gypsum pond water, overflow cannot be discharged without treatment.

In general terms, the Development Document recommends three treatment measures for the operation of wet process phosphoric acid plants:

1. Collection, containment, and neutralization of the intermittent leaks from the sulfuric acid plant;

2. Lime treatment and clarification of the gypsum pond overflow to precipitate phosphates and fluorides as their calcium salts;

3. Installation of a seepage control system. The seepage control system is intended to collect seepage from the perimeter of the pond and to then return it to the pond. Seepage control in itself does not result in a wastewater stream, but by adding to the overall pond water inventory, can cause the overflow stream to increase in size.

Based on an assumed gypsum pond overflow rate (as delineated in the Development Document), an estimation of the volume and characteristics of both the raw gypsum pond water and the treated overflow effluent is presented in Table IV-7.

The wastewater treatment system will produce a waste sludge containing calcium fluoride and calcium phosphate salts.

TABLE IV-7

WET-PROCESS PHOSPHORIC ACID WASTEWATER CHARACTERISTICS

Basis: 50,000 tpy (P_2O_5)

Wastewater Characteristics	Gypsum Pond Raw Wastewater		Treated Effluent	
	(mg/1)	(lb/day)	(mg/1)	(lb/day)
Total suspended solids	No Data	No Data	20	36
Phosphorus (P_4)	-	-	-	-
Phosphate (PO_4^{-3})	15,000	27,600	20	36
Sulfate (SO_4^{-2})	~2,000	3,600	~2,000	3,600
Fluoride (F^-)	8,500	15,300	15	27
Total acidity (as $CaCO_3$)	No Data	No Data	0	0
Wastewater Flow Rate	0.216 mgd		0.216 mgd	

Note: The above wastewater flow rates and waste loadings are based on the assumption that there will be a gypsum pond overflow.

Source: Arthur D. Little, Inc., estimates, based on " . . . Development Document for Phosphorus Derived Chemicals . . .", US EPA.

It is estimated that wastewater treatment sludge will be generated at the rate of 45,500 tpy @ 10% solids. Since the gypsum pond is available for storage, in most cases it would be feasible to pump the wastewater treatment sludge into the pond. The resultant sludge-disposal costs would be lower than if the sludge had to be hauled to an offsite disposal area.

Wastewater treatment cost estimates, based on the previously described treatment system, are presented in Table IV-8.

b. Air Pollution

Both the digestion system and the evaporation system produce vent gas streams which contain both P_2O_5 particulates and fluorine. The fluorine distribution in the system is illustrated by the material balance presented in Figure IV-4. The normal fluorine content of phosphate rock is about 3-1/2%. Of this fluorine, 30% appears as part of the product acid at a rate of about 60-70 lb of fluorine/ton of P_2O_5. About the same quantity is discharged, along with the gypsum filter cake, to the settling pond. Some 16% of the original fluorine is evolved in the digesters and 24% in the evaporator stack. It is not difficult to recover this fluorine by wet scrubbing,

TABLE IV-8

WET-PROCESS PHOSPHORIC ACID WASTEWATER TREATMENT COSTS

Basis: 50,000 tpy P_2O_5

	TOTAL PLANT
CAPITAL INVESTMENT	$292,000
DIRECT OPERATING COST	
Labor (including overhead)	48,700
Maintenance (labor and materials)	11,700
Chemicals	87,800
Electricity (@ $0.020/kwh)	13,300
Sludge Disposal	91,000
TOTAL DIRECT OPERATING COST	$252,500
INDIRECT COSTS	
Depreciation (@ 9%)	26,300
Return on Investment (@ 20%)	58,400
Taxes and Insurance (@ 2%)	5,800
TOTAL INDIRECT COST	$ 90,500
TOTAL ANNUAL COST	$343,000
UNIT COST ($/ton as P_2O_5)	$6.86

Notes:

1. Treatment consists of:
   a) Sulfuric acid plant leakage containment system.
   b) Gypsum pond seepage control, and
   c) Lime treatment and clarification of gypsum pond overflow water.
2. Capital investment adjusted to March 1975 level (ENR=2126).
3. Quantities:
   - Labor - 3960 man hour/yr @ $12.30/man hour (with OHD),
   - Chemicals - 2700 tpy hydrated lime @ $32.50/ton,
   - Electricity - 666,000 kWh/yr @ $0.020/kWh,
   - Sludge - wastewater treatment sludge - 45,500 tpy (wet basis) (sludge disposal on-site @ $2.00/wet ton)

Source: Arthur D. Little, Inc., estimates.

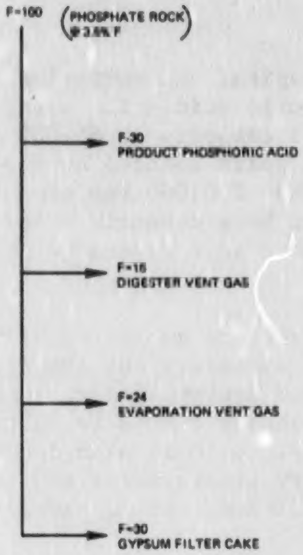


Figure IV-4. Fluorine Material Balance - Wet-Process Phosphoric Acid

although the chemistry is complicated by the presence of silica. In the vent gases fluorine exists as hydrogen fluoride and silicon tetrafluoride gas. The hydrogen fluoride dissolves readily in the scrubber water to make hydrofluoric acid solution and the silicon tetrafluoride reacts with water to form fluosilicic acid and precipitate silica:

$$(3SiF_{4(g)} + 2H_2O \xrightarrow{H_2O} 2H_2SiF_{6(sol)} + SiO_2\downarrow).$$

The equipment must be shut down and cleaned at rather frequent intervals to control this formation of silica. At some plants the fluosilicic acid can be recovered either as the acid or as the sodium or potassium salt. In a majority of plants, however, this stream is pumped to the settling pond and contained there.

3. Energy Requirement

Purchased electricity is the major energy requirement for the wet process phosphoric acid system and is required at about 250 kWh/ton of P_2O_5. It is used to drive pumps, agitators, filters and similar machinery, including for the circulation of cooling water. If the plant were not integrated with an onsite sulfuric acid plant, it would be necessary to use fuel to raise substantial amounts of steam, primarily for concentration of the acid from 32% filtrate to 54% as product. The recoverable energy in the sulfur burned amounts to about 13 million Btu/ton of P_2O_5. About half of the steam equivalent of this heat is used for turbine drives in the sulfuric acid plant and the other half for evaporation and other needs in the phosphoric acid plant.

4. Economic Factors

Table IV-9 presents the capital and operating costs of a wet process plant for production of phosphoric acid. The plant is assumed to be located in the midwest and operate at a capacity of 50,000 tpy of P_2O_5. This is a small capacity compared to new units located at phosphate centers, such as Florida, where plants larger than 200,000 tpy are common. The smaller size has been chosen because it does have economic viability, and is a good match for onsite use of phosphoric acid in a system to produce purified phosphate for the detergent industry.

Capital costs for this plant are estimated at $10,200,000. This figure includes processing facilities necessary for grinding phosphate rock to the size desirable for the digestion system, and the digestion, filtration, and evaporation sections of the phosphoric acid facility. The cost of the unit for converting sulfur to sulfuric acid is also included. The investment of $10,200,000 includes the battery limits plant and necessary site development and auxiliary and storage facilities. It is based on 1975 construction costs.

Raw materials required are phosphate rock and sulfur. Dry Florida rock at 30% P_2O_5 is used and the price of $30/ton includes shipping to the midwest plant site. This price represents our best judgment in today's volatile market. Recovery of P_2O_5 as acid amounts to better than 95% of the phosphate in the raw material. Sulfur is assumed to be obtained from the Gulf Coast and delivered at about $45/ton. These raw materials are the most significant cost elements.

Electric power consumption amounts to 250 kWh/ton of P_2O_5, about one-third of this being required for grinding of phosphate rock. This is a large power requirement, but not an unusually heavy industrial load and the plant can be expected to pay about the average price for electricity which was about 2¢/kWh in 1975.

There is a small process water requirement for manufacture of sulfuric acid and an additional water requirement for phosphoric acid. Together these stoichiometric requirements amount to about 0.6 thousand gal/ton of P_2O_5 product. The total water requirement of 4.3 thousand gal/ton also includes recycled water required for slurrying and disposal of the gypsum, and for makeup streams to the scrubbing towers for the digestion and evaporation systems. Labor requirements have been calculated on the basis of a staff of about eight operators/shift, plus one shift supervisor. The maintenance labor staff is a little smaller. Maintenance labor and materials together are estimated at an annual cost equal to 6% of the capital investment. The depreciation cost of about $18/ton of P_2O_5 has been estimated on the basis of an 11 year life of the facility. Total cost of manufacture is about $213/ton of P_2O_5.

TABLE IV-9

ESTIMATED COST OF PHOSPHORIC ACID MANUFACTURE

Product: Phosphoric Acid

Process: Wet-Process (Phosphate Rock + H_2SO_4)

Location: Midwest

Fixed Investment: $10,200,000

Annual/Design Capacity: 50,000 tons P_2O_5

Annual Production: 50,000 tons P_2O_5

	Units	Price ($/unit)	Requirement (Units/ton P_2O_5)	Cost ($/ton P_2O_5)
Variable Costs				
Raw Materials				
Phosphate rock (30% P_2O_5)	tons	30.00	3.49	104.70
Sulfur	tons	45.00	0.84	37.80
Energy				
Electricity	kWh	0.020	250.0	5.00
Water	mgal	0.03	4.3	0.13
Labor				
Direct operating labor	Man-yr	15,000	7×10^{-4}	10.50
Direct supervision	Man-yr	20,000	1×10^{-4}	2.00
Maintenance	3% CI			6.12
Maintenance Material	3% CI,			6.12
Labor Overhead	30% Labor			5.59
Total variable costs				177.96
Fixed Costs				
Plant overhead	70% Labor			13.04
Local taxes & ins.	2% CI			4.08
Depreciation	9% CI			18.36
Total cost of manufacture				213.44
20% return on investment (pretax)				40.80
Pollution control				6.86
				261.10

D. PROBLEMS RELATED TO PROCESS CHANGE AND INDUSTRY GROWTH

1. Pollution Control

The problems of pollution control in the elemental phosphorus and the wet process phosphoric acid systems have been the subjects of extensive studies in the EPA guidelines work. This work is most detailed in the case of aqueous effluents, but considerable attention has also been given to air pollution and to sludge disposal problems. The major air pollution problems, common to both processes, concern elimination of fluorine and dust. In the case of the wet process plants, aqueous streams, including waste scrubber liquor, can usually be handled in containment basins. The location of the electric furnace plants on the other hand, particularly in the western states, is such that the handling of aqueous effluents represents a difficult problem.

2. Shortage and Escalating Cost of Electricity

The electric furnace process for conversion of phosphate rock to elemental phosphorus requires a power input of about 13,000 kWh/ton of phosphorus which makes it one of the most intensive users of electricity among the electric furnace industrial operations. In addition, the industry has progressed to the point where the size of single furnace installations is now at least 40,000 kW. This industry grew in Tennessee at about the same time as the rapid development of the TVA, and to a large extent these growths were synergistic. Phosphorus requires power in large blocks, and thus a commitment to use the power provided the utility with an assured outlet for a major part of each increment of expansion. The electrical characteristics of the phosphorus furnace are such that it can be interrupted for relatively long periods without any damage other than the loss of the phosphorus production. TVA utilized this feature to offer interruptible power contracts at favorable rates, thus, in effect, utilizing the phosphorus customer as a peak-shaving facility. In a similar manner, the electric furnace operations in Idaho and Montana were developed on the basis that electricity would be available in abundant supply and at economical rates, largely derived from hydroelectric power. In recent years the availability of this electricity has markedly diminished and the expansion of the electric furnace industry has been held back largely because of a fear that sufficient power would not be available. This has been dramatically illustrated by the fact that the Stauffer plant in Montana has not been able to run at more than a fraction of its capacity because of the allotment of Bonneville power.

3. High Capital Cost of Incremental Capacity

An additional deterrent to expansion of electric furnace phosphorus is the capital cost of a single furnace required for such an expansion. If such an expansion were to occur today, it would probably be based on a furnace with a capacity of 60,000 kW and a capital investment of about $25 million. Such an investment is extremely risky in view of the doubtful availability and uncertain price of the electricity required to operate the furnace.

4. Economic Availability of Suitable Ore

The analysis and physical characteristics of available deposits of phosphate rock, to a degree, have influenced the type of conversion practiced. The wet process requires rock in a state of subdivision which will disperse readily in the digestion slurry and have good reactivity with the acid. A number of impurities are present in phosphate minerals, such as iron and aluminum salts, carbonates, and organic matter, which cause difficulty in the wet-process system. The carbonate evolves CO_2, and the organic matter creates foam and makes a dark colored acid. The presence of impurities of this type increases the size of the digestion system, and requires expensive special measures for their control. The presence of iron and aluminum makes filtration of the resultant gypsum slurry difficult. A relatively fine rock is desired to increase the surface area available for reaction. The phosphate content of the rock varies among deposits. A relatively high grade at 30-35%

P_2O_5 has been economically available and most phosphate rock for wet-process acid has been based on this type of material. Deposits of this type of phosphate rock are abundant in central Florida and have been the basis for the growth of the industry in that state. In addition to production of phosphoric acid and derivatives in Florida, the rock is exported through the Port of Tampa for shipment elsewhere in the United States notably throughout the midwest on the Mississippi River system. There is also a very large and vital trade of phosphate rock for export to foreign countries.

In Tennessee, deposits of this grade of phosphate rock have largely been mined out and the remaining deposits are of lower grade and cannot compete with the Florida rock for wet-process systems. Over the years a sizeable electric furnace phosphorus industry has grown in Tennessee based on the availability of cheap electric power from the TVA. This industry utilizes the Tennessee rock which must first be processed by calcining and agglomeration to a size suitable for feed to the phosphorus electric furnace. Escalating costs of both rock and electricity make expansion of the industry in Tennessee doubtful for either process.

The other major U.S. deposit is in the Mountain States in the West, predominantly in Idaho, Montana, Wyoming, and Utah. Two types of deposits exist. One is a rich high-grade deposit existing in thick seams, but at depths suitable only for underground methods, and the second consists of deposits which exist in relatively thin seams at shallow depths, uplifted at fairly steep angles which can be exploited by strip mining. An extensive strip mining industry exists at present in southeastern Idaho and western Wyoming and is the source of most of the western rock currently in use. The western rock is of a grade which can be used directly in the electric furnaces without beneficiation. A smaller percentage of the western rock, perhaps 25% to 33%, is currently used in wet process plants in the western states. The higher grade and more suitable eastern rock cannot compete in this location because of the cost of shipment.

V. PROCESS OPTIONS

A. OPTIONS TO BE ANALYZED IN DEPTH

The use of phosphate and phosphorus compounds for fertilizers, detergents, and industrial chemicals is increasing and expansion of production appears to be certain. For a number of reasons, as detailed earlier, there are strong pressures to bring about this expansion without the commitment to additional electric furnace capacity. A significant part of the expansion may be via wet-process acid, purified to the degree necessary for use in some of the furnace-grade outlets.

An estimate of current and future markets for products important to this analysis is presented in Table V-1. Current use of phosphoric acid in detergents is estimated to be 600,000 tpy of P_2O_5, or about 40% of the total use of clean phosphoric acid. In 10 years this application is expected to increase to about 900,000 tpy and maintain its share of the total demand. Thus, it is apparent that there is ample opportunity for adoption of a clean wet-process acid even though that process does not purify the acid to food-grade specifications.

TABLE V-1

INDUSTRIAL PHOSPHATE DEMAND
(000 tons P_2O_5)

	1975	1985
Phosphoric Acid Derivatives		
Detergents	600	900
Food and fine chem.	240	400
Phosphoric acid (furnace)		
Direct use	120	200
Fertilizer	115	0
Elemental phosphorus and non-acid uses	165	200
Phosphorus exports	45	40
Unaccounted for	100	100
	1385	1840
Nominal Phosphorus capacity	1354	

Source: Arthur D. Little, Inc., estimates.

Two methods of cleanup have been demonstrated commercially. One is a chemical method which involves neutralization and precipitation of the impurities; the second is a solvent extraction system. These options, as they pertain to detergent grade phosphates, are summarized below and described in detail in Sections V-B and V-C.

Purification to food-grade specification is possible and has been demonstrated, but it is quite complicated and expensive. Sufficient furnace acid will be available for food-grade products if some detergent production is switched to wet-process acid. The results of this work are reported in a later section of this report.

We feel that there is a strong likelihood that several such units will be built in the near future.

1. Solvent Extraction Cleanup of Wet-Process Phosphoric Acid

The solvent extraction system begins with conventional digestion of phosphate rock with mineral acid to produce an aqueous solution of H_3PO_4. An immiscible organic solvent is used to extract P_2O_5, and a clean aqueous phosphoric acid is regenerated by contacting with water. Such a system was proposed on a number of occasions, and we believe several companies have pursued research on the method. It was developed, patented, and commercialized by Israeli Mining Industries, Ltd. (Baniel et al, 1962; I.M.I., 1963; "Hydro-chloric-Based Route ....," 1962). The IMI process employs hydrochloric acid as a digestion agent and butyl alcohol as the solvent. A small plant was built at Haifa and commercial units built and operated in Japan and Mexico. In North America, Kaiser proposed such a unit in Louisiana ("Hydrochloric-Based Route ...", 1962), and Dow at Sarnia in Ontario ("Dow to Test ... ", 1963). Kaiser's plant was never built. Dow's unit was a pilot plant and Dow has not pursued this opportunity to our knowledge. Interest in this unit has been based on possible improvement in economics, and on operation in conjunction with a plant producing hydrochloric acid as a waste material. These incentives remain and are strengthened by pressing needs for additional phosphate capacity and the dwindling availability and rising cost of electric power.

2. Byproduct Sulfuric Acid for Wet-Process Phosphoric Acid

In the conventional wet process for phosphoric acid, sulfur is a raw material and is converted to sulfuric acid at the site of the phosphoric acid plant. The emphasis on SO_2 control in utility plant stacks presents the opportunity to manufacture sulfuric acid as a byproduct at the electric power station. A possible outlet for this sulfuric acid would be a phosphoric acid plant which could be located at the utility site to convert phosphate rock shipped from the phosphate mine. One such location is Tampa, Florida, where there is strong pressure for better SO_2 control, and which is only 50 miles from the phosphate source in Polk County. As currently practiced, burning sulfur at the phosphoric acid plant results in byproduct steam at a rate ample for the needs of the phosphoric acid unit. If sulfuric acid is substituted for sulfur, this energy would have to be made up by the independent generation of steam. A major fraction of this steam requirement is devoted to concentration of the 30% P_2O_5 phosphoric acid produced in the digestion system to the 54% strength required for shipment or use as fertilizer acid.

3. Strong Phosphoric Acid Processes

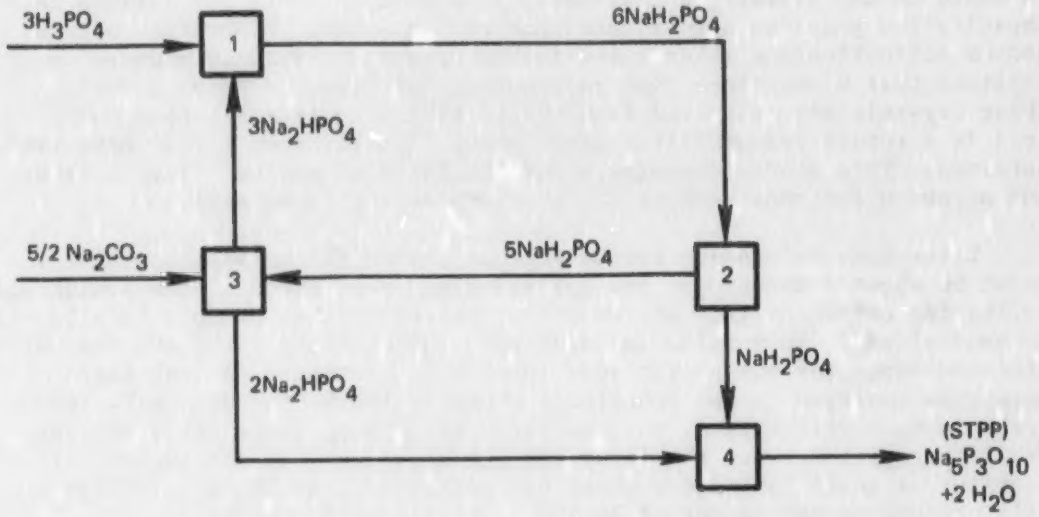
There are now at least two processes for modification of the wet process system so that acid of 50% strength may be produced directly without the need for evaporation, thus eliminating the need for steam. One such system has been developed by Fisons (Crerar, 1973; Blumrich) and commercial units have been built and are operating in Holland and in Yugoslavia. The opportunity for practice of this strong acid system either in conjunction with a conventional sulfur-based plant or in a plant supplied with by-product sulfuric acid has been analyzed in a later section of this report.

B. CHEMICAL CLEANUP OF WET-PROCESS PHOSPHORIC ACID

1. Process Description

As stated in Chapter IV, there are a number of impurities in wet-process phosphoric acid which make it unsuitable for uses such as detergent phosphate. These impurities include calcium chloride, iron and aluminum salts, carbon and organic matter, and small quantities of a number of heavy metals, such as magnesium, chromium, titanium, manganese, copper, zinc, arsenic, vanadium, and uranium. The acid is saturated in calcium sulfate and has a high content of fine suspended solids. It is difficult to remove these impurities to the degree necessary to meet specifications for food-grade or fine-chemical phosphate use. A major outlet for phosphoric acid, however, is in the form of sodium tripolyphosate (STPP). Wet-process acid can be purified to the degree necessary for this product by a two-stage neutralization (Van Wazer, Jr., 1961). A major impurity which precipitates upon neutralization is sodium silicofluoride and, if the first step of neutralization is stopped at a pH of about 2, the precipitate is relatively pure and can be readily separated by filtration. The second stage neutralization completes the reaction to the stoichiometric equivalent of monosodium phosphate at a pH of about 5. Iron and aluminum phosphates are insoluble under these conditions and precipitate, along with the remaining sodium silicofluoride. The use of chemical dosing agents, such as barium carbonate and sodium sulfide, at this stage can eliminate the sulfate as barium sulfate, and the heavy metals as the sulfides. This dosing may not be required with some phosphate rock raw materials. The process has been described in a qualitative way in a number of literature references, but there is little quantitative data on its application. For purposes of this report, we have prepared the process outline as illustrated in the accompanying flowsheet and a material and energy balance to permit evaluation of the system.

STPP is made by drying and calcining a solution stoichiometrically equivalent to a mixture of one mole of monosodium phosphate and two moles of disodium phosphate. The objective is to supply sodium phosphate solutions at about 50% concentration in the purity required for STPP manufacture. A simplified diagram of this process is illustrated below.



In step 1, three moles of phosphoric acid are neutralized with three moles of disodium phosphate to form six moles of monosodium phosphate. In step 2, 1/6 of this salt is separated as product and the remainder recycled to neutralization in step 3. Two-and-one-half moles of sodium carbonate, the primary neutralizing agent, are mixed with the recycled monosodium phosphate to form five moles of disodium phosphate. Three moles of disodium phosphate are recycled for step 1 and the remaining two form the disodium phosphate product sent to the STPP operation.

It would be possible to neutralize phosphoric acid directly with sodium carbonate, and some descriptions of the purification process are based on this method. The result, however, would be a strong evolution of CO_2 and, in the early stages of reaction, a danger of carrying off an acidic mist with undesirable loss of fluorine as HF or SiF_4. In the latter stages of neutralization, a highly alkaline local concentration would result if sodium carbonate were added directly, and would produce gelatinous precipitates very difficult to separate by filtration. With the method diagrammed above, neutralization is accomplished after the impurities have been removed and without any precipitation during neutralization.

The flowsheet presented in Figure V-1 is based upon production of sodium salts equivalent to 50,000 tpy of P_2O_5. At an operating factor of 330 stream days/year, the feed rate is about 40,000 lb/hr of 32% P_2O_5 crude phosphoric acid from the wet-process system. This stream is mixed with recycled disodium phosphate solution at about 14,000 lb/hr in the primary neutralizer. The crude acid is stoichiometrically deficient in silica to precipitate the fluorine, and additional silica at the rate of 130 lb/hr is added to the primary neutralizer. This unit is about 500 gallons in capacity and provides a residence time of 5 minutes. Separation of the sodium silicofluoride takes place in the primary crystallizer where we estimate that a residence time is required for proper crystal growth. These crystals are separated from the partially neutralized phosphoric acid in a rotary vacuum filter where about 1600 lb/hr of filter cake are obtained. This sludge contains about 475 lb/hr of sodium silicofluoride and accounts for about 75% of the fluorine in the crude acid.

Literature references recommend that the pH of the solution at this point be about 2 for proper precipitation and separation of the sodium silicofluoride cake. At this pH, about 30% of the initial phosphoric acid will be neutralized. This value is based upon calculations using the dissociation constants for phosphoric acid in dilute solutions. At the ionic strengths employed in the commercial process, there is undoubtedly some error in this calculation, but the error affects only the split of neutralizing agent between the first and second stages and not the overall results. A rough laboratory check has confirmed that the neutralization will proceed to the extent of 30-40% of the initial phosphoric acid.

Prior to completion of the neutralization, barium carbonate is added in a secondary dosing tank to react with sulfate in solution to form and precipitate barium sulfate. In the material balance as presented, a total of 1135 lb/hr of barium sulfate is obtained and this material is the major constituent of this second filter cake. The treated slurry is then pumped to the second neutralizer where it reacts with about 33,000 lb/hr of disodium phosphate solution. At this point, the phosphoric acid has been entirely neutralized to monosodium phosphate and the pH is stated to be about 5. Under these conditions, heavy metals can be precipitated as the sulfides and removed with the second stage filter cake. As in the first stage, a residence time of about 5 minutes is provided in the neutralizer and about 60 minutes in the crystallizer. These conditions require a nominal volume of about 1000 gallons for the neutralizer and about 10,000 gallons for the crystallizer. Sludge from the second-stage filter amounts to about 7300 lb/hr and contains about 2200 lb of solids on a dry basis. Characteristics and disposal of these and other effluent streams is discussed below. After filtration, the monosodium phosphate solution is divided, and 83.3% of it is treated with soda ash. We estimate that a residence time of 30 minutes is required here and a volume of 3000 gallons is needed. Sodium carbonate at a rate of about 14,000 lb/hr is added to this tank and carbon dixoide at about 6000 lb/hr is vented to the stack.

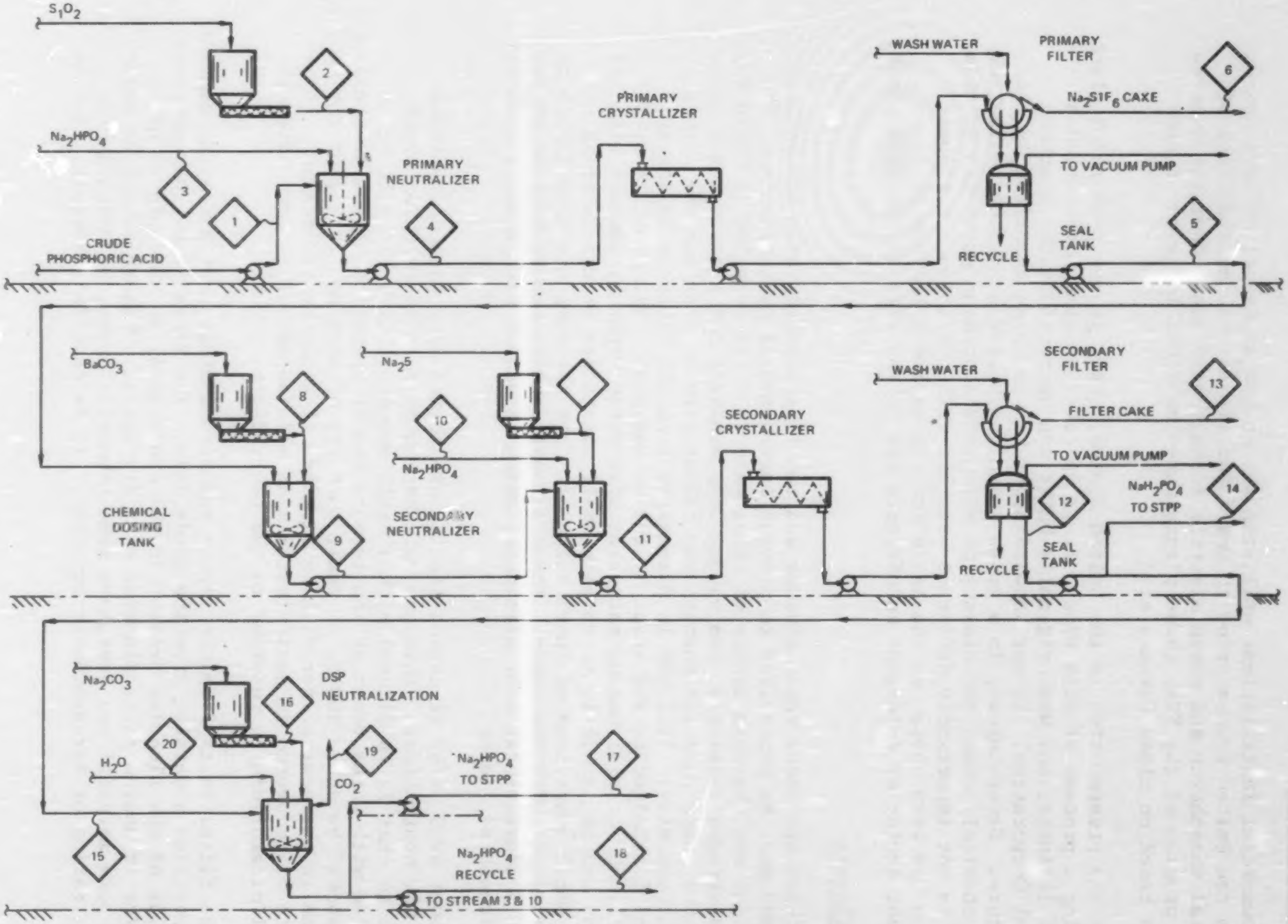

S_1O_2
2
Na_2HPO_4
3
1
CRUDE PHOSPHORIC ACID
PRIMARY NEUTRALIZER
4
PRIMARY CRYSTALLIZER
WASH WATER
PRIMARY FILTER
6
Na_2SiF_6 CAKE
TO VACUUM PUMP
RECYCLE
SEAL TANK
5
$BaCO_3$
8
CHEMICAL DOSING TANK
9
Na_2S
10
Na_2HPO_4
SECONDARY NEUTRALIZER
11
SECONDARY CRYSTALLIZER
WASH WATER
SECONDARY FILTER
13
FILTER CAKE
TO VACUUM PUMP
12
RECYCLE
SEAL TANK
NaH_2PO_4 TO STPP
14
Na_2CO_3
16
DSP NEUTRALIZATION
20
H_2O
19
CO_2
15
Na_2HPO_4 TO STPP
17
Na_2HPO_4 RECYCLE
18
TO STREAM 3 & 10

Figure V-1. Flow Sheet-Chemical Cleanup of Wet-Process Phosphoric Acid

2. Current Status

Commercial installations utilizing the method as described were operated in the United States prior to World War II. As the availability of elemental phosphorus and clean electric furnace acid grew under the impetus of the program of the TVA, these plants were abandoned in favor of production based on clean furnace acid.

At the present time in the United States, there is one commercial plant utilizing a process of this type. It is operated by Olin Corporation at Joliet, Illinois, and was originally built and operated by the Blockson Chemical Corporation. To our knowledge, it has not been described in the literature. Nevertheless, in a gross sense, we believe that the evaluation of the chemical method for cleanup of wet-process acid as presented in this report is not importantly different from the Olin operation. A midwest location has been chosen as the basis for our estimate because it is an important center of detergent manufacture and is the site of the Olin plant.

3. Effluents

There are three vapor streams and two filter cakes which are effluents, and these must be controlled to prevent environmental contamination. The quantities and characteristics of these materials are detailed in Table V-2. The gas streams consist of two vacuum pump exhausts and a neutralizer vent. The vacuum pumps pull air through the filter cake to displace the liquor which it contains. This air is disengaged from the filtrate in the seal tank and discharged to the stack by the vacuum pump. The quantity of air is small, but it will become saturated with water vapor by contact with the filtrate and it is likely to entrain small quantities of the filtrate as a mist. Small quantities of lubricating oil from the pump are also likely to be carried off with the vapor. These exhaust streams can be handled at low cost in a conventional mist eliminator which is washed with a small quantity of recirculated liquor.

About 5900 lb/hr of carbon dioxide are formed as a gaseous byproduct in the DSP neutralizer. This gas will be vented to a stack under draft control so that it is diluted with a small amount of air. It will be saturated with water vapor at the temperature of operation of the neutralizer which should be about 100°F. A small quantity of mist consisting of the solution in the neutralizer will be carried off with the gas stream. This mist can be recovered in an irrigated mist eliminator. The liquor from the mist eliminator can be returned to the neutralizer.

The filter cakes from the first- and second-stage neutralization contain the impurities separated from the crude acid. The first stage cake contains about 75% of the fluorine present in the crude acid, and amounts to about 475 lb/hr of sodium silicofluoride on a dry basis. This salt will be relatively pure material and does have some commercial uses, principally for water treating or for synthetic cryolite. It is doubtful, however, that it

TABLE V-2

PROCESS EFFLUENTS CHEMICAL CLEANUP OF WET-PROCESS PHOSPHORIC ACID
Operating Rate: 50,000 tpy P_2O_5

Gas Streams

Vacuum Pump Exhaust - Primary Filter

Rate: 200 scfm Temperature: 100°F

Composition: Air
H_2O Vapor - saturated
Mist - from contact with 24% H_3PO_4, 21% NaH_2PO_4 at pH=2

Vacuum Pump Exhaust - Second Stage Filter

Rate: 200 scfm Temperature: 100°F

Composition: Air
H_2O Vapor - saturated
Mist - from contact with 49% NaH_2PO_4, pH=5

Neutralizer Vent

Rate: 900 scfm Temperature: 100°F

Composition: CO_2 - 5917 lb/hr
Air - Minor
H_2O Vapor - saturated
Mist - from contact with 50% Na_2HPO_4, pH=5

Liquid Streams None

Solid Streams (Sludge)

First Neutralization Cake

Solids Content: 30%

Rate: 475 lb/hr (dry basis)

Composition: Na_2SiF_6

Minor Impurities - H_3PO_4, NaH_2PO_4, $CaSO_4$, $FePO_4$, $AlPO_4$

Trace Impurities - Mg, Mn, K, CR, Ti, U, V, As

Second Neutralization Cake

Solids Content: 30%

Rate: 2195 lb/hr (dry basis)

Composition:

Na_2SiF_6 -	158 lb/hr
$FePO_4$ -	607
$AlPO_4$ -	67
$BaSO_4$ -	1135
Other -	228
	2195 lb/hr

Trace Impurities - Mg, Mn, K, CR, Ti, U, V, As

Source: Arthur D. Little, Inc., estimates.

could be economically marketed from this plant, and it is more likely that the sludge will be pumped to a settling pond and treated along with the gypsum slurry and scrubber effluents from the wet-process acid plant. There are one or two plants processing these fluids for recovery of fluorine compounds for use in aluminum manufacture, but alternate sources of fluorides, such as old "pot-linings," are much cheaper.

The second-stage cake contains less sodium silicofluoride, and its major constituents are the iron and aluminum and other impurities precipitated from the acid at this stage. In our material balance, we have shown a large quantity (1135 lb/hr) of barium sulfate in this cake. In some wet-process plants, the quantity of sulfate present in the crude acid is less than shown here, and the requirement for barium can be reduced or even eliminated. Barium is nominally used at its stoichiometric requirement, and the solubility of barium is low. The possibility of barium ion in the effluent must, nevertheless, be recognized. The metallic elements listed as trace impurities are derived from phosphate rock. They occur in similar small amounts in the effluent streams from the wet-process system and in the slag from elemental phosphorus production. In these processes, they have not been cited as harmful pollutants. We do not anticipate that any special measures for their control will be necessary in this process.

a. Water Pollution Control

Aside from the previously described neutralization filter cakes (which are really considered a waste sludge rather than a wastewater stream), there are no major wastewater streams discharged from the chemical cleanup step. The volume and characteristics of the treated effluent from the entire phosphoric acid production and purification unit are essentially the same as the base line wet process plant described in Chapter IV. The effluent characteristics are shown in Table V-3.

For the purpose of cost comparison, it is assumed that the neutralization filter cakes will be deposited in the gypsum pond and that the cost will be accounted for under sludge disposal. Wastewater treatment cost estimates are presented in Table V-4. The treatment costs are essentially the same as without the cleanup step, with the exception of the additional sludge disposal cost due to the neutralization cake.

4. Energy

Electricity is the only energy requirement for this process. We have summarized the major motors and drives required by the process; about 103 connected horsepower are required. We estimate that an electric load of 100 kW would result; this would be equivalent to 16 kWh/ton of P_2O_5 processed.

No steam and no energy for heating or cooling are required. The process operates at ambient temperature and the heats of reaction are small.

TABLE V-3

WET-PROCESS PHOSPHORIC ACID PLUS CHEMICAL CLEANUP WASTEWATER CHARACTERISTICS

Wastewater Characteristics	Gypsum Pond Raw Wastewater		Treated Effluent	
	(mg/l)	(lb/day)	(mg/l)	(lb/day)
Total suspended solids	No data	No data	20	36
Phosphorous (P_4)	-	-	-	-
Phosphate (PO_4^{-3})	15,300	27,600	20	36
Sulfate (SO_4^{-2})	~2,000	3,600	~2,000	3,600
Fluoride (F^-)	8,500	15,300	15	27
Total acidity (as $CaCO_3$)	No data	No data	0	0
Wastewater Flow Rate	0.216 mgd		0.216 mgd	

Note: The above wastewater flow rates and waste loadings are based on the assumption that there will be a gypsum pond overflow.

Source: Arthur D. Little, Inc., estimates, based on " . . . Development Document for Phosphorus Derived Chemicals . . .", U.S. EPA.

TABLE V-4

WET-PROCESS PHOSPHORIC ACID PLUS CHEMICAL CLEANUP WASTEWATER TREATMENT COSTS
(Basis: 50,000 tpy P_2O_5)

CAPITAL INVESTMENT	$292,000
DIRECT OPERATING COST	
Labor (including overhead)	48,700
Maintenance (labor & materials)	11,700
Chemicals	87,800
Electricity (@ $0.020/kWh)	13,300
Sludge Disposal	
a. Wastewater treatment sludge	91,000
b. Phosphoric acid purification sludge	70,400
TOTAL DIRECT OPERATING COST	$322,900
INDIRECT COSTS	
Depreciation (@ 9%)	$ 26,300
Return on investment (@ 20%)	58,400
Taxes and insurance (@ 2%)	5,800
TOTAL INDIRECT COST	$ 90,500
TOTAL ANNUAL COST	$413,400
UNIT COST ($/ton as P_2O_5)	$8.27

Notes: 1. Treatment consists of:

a. Sulfuric acid plant leakage containment system
b. Gypsum pond seepage control
c. Lime treatment and clarification of gypsum pond overflow water

2. Capital investment adjusted to March 1975 level (ENR - 2126)

3. Quantities:

- Labor - 2960 man-hour/yr @ $12.30/man-hour (with OHD)
- Chemicals - 2700 tpy hydrated lime @ $32.50/ton
- Electricity - 666,000 kWh/yr @ $0.020/kWh
- Sludge - a. Wastewater treatment sludge - 45,500 tpy (wet basis)
  b. Purification sludge - 35,200 tpy (wet basis)
  (Sludge disposal on-site @ $2.00/wet ton)

5. Economics

Cost of chemical cleanup of wet-process phosphoric acid has been estimated on the basis of the flowsheet and material balance previously described. On the basis of this equipment list, we have estimated the capital investment at \$1,200,000. The estimate includes a process building at \$100,000 and an allowance for offsite facilities at 20% of the battery limits cost.

In Table V-5 we present an estimate of the operating cost for the chemical cleanup method. The resulting cost of manufacture is \$240/ton of P_2O_5 as the mixed sodium salt. This cost is \$30 for more than the cost of P_2O_5 as the crude acid and represents the cost of operating the cleanup section. For this estimate we have used the cost of crude acid manufactured at 54% P_2O_5 strength, less about \$3 allowance for the cost of the evaporation step which would not be required. A requirement of about 1.1 tons of soda ash/ton of P_2O_5 is shown in the table, but with no charge for the soda ash. The estimate has been prepared in this manner to permit comparison of a clean acid cost with comparable material by the electric furnace route; the cost of the soda ash is a cost element in the conversion of acid to STPP. The chemical treatment and the cost of the chemicals for cleanup of the acid have been based on complete removal of the sulfate as barium sulfate. The result is a charge for barium carbonate which amounts to \$18/ton of P_2O_5 and is almost two-thirds of the total cost of cleanup of the acid. The necessity for this step depends both upon the nature of the crude acid and the phosphate rock from which it is made and upon the specifications for the detergent end-use. The precipitation of barium sulfate at this step helps to make the precipitate more readily filterable, but cheaper filter aids could probably be utilized. The results of this calculation illustrate the sensitivity of the economics to the chemical dosing actually required for adequate cleanup. Other chemical costs for silica and sulfide are minor. Electricity and water are also insignificant costs.

The plant is operated with two men/shift and with one man for direct supervision. The labor charge, including maintenance labor, is about \$4.20/ton of P_2O_5. Major items of fixed cost are plant overhead, which at 70% labor is about \$2.50, and depreciation at an 11-year life with a charge of a little over \$2.00/ton of P_2O_5.

6. Assessment

The estimates presented in this report indicate a cost of about \$240/ton of P_2O_5 as purified wet-process acid, as compared to a cost of about \$213/ton of acid derived from elemental phosphorus. The difference between these figures is well within the accuracy of the estimating methods employed, and we believe that the methods are economically competitive. Actual sales on fair transfer value must include an allowance for return on investment; the capital cost of the electric furnace is so high that this return reverses the economics and makes the price of furnace acid more than that of clean wet-process acid.

TABLE V-5

OPERATING COST OF CHEMICAL CLEANUP

Location: Midwest

Annual/Design Capacity: 50,000 tons P_2O_5

Fixed Investment: $1,200,000

Annual Production: 50,000 tons P_2O_5

	Units	Price $/Unit	Units/ton P_2O_5	Cost $/ton P_2O_5
VARIABLE COSTS				
Raw Materials & Chemicals				
32% P_2O_5 acid	tons P_2O_5	210(1)	1.0	210.00
Na_2CO_3	tons	N.C.(2)	1.13	N.C.(2)
SiO_2	lb	0.008	22.7	0.18
$BaCO_3$	lb	0.12	152	18.24
Na_2S	lb	0.15	2.5	0.38
Energy				
Electricity	kWh	0.020	16	0.32
Water	10^3 gal	0.03	1	0.03
Labor				
Direct Operating Labor	man-yr	15,000	2×10^{-4}	3.00
Direct Supervision	man-yr	20,000	2×10^{-5}	0.30
Maintenance Labor	man-yr	15,000	6×10^{-5}	0.90
Maintenance Material	2% of CI			0.48
Labor Overhead	30% Labor			1.13
TOTAL VARIABLE COST				234.96
FIXED COSTS				
Plant Overhead	70% Labor			2.65
Local Taxes & Ins.	2% of CI			0.48
Depreciation	9% of CI			2.16
TOTAL COST OF MANUFACTURE				240.25
Return on Investment (pretax) -				
Wet-Acid Plant				40.80
Cleanup System				4.80
POLLUTION CONTROL				8.27
TOTAL				294.12

(1) At cost of 54% P_2O_5 acid less $3

(2) Soda ash is chargeable to STPP operation.

Source: Arthur D. Little, Inc., estimates.

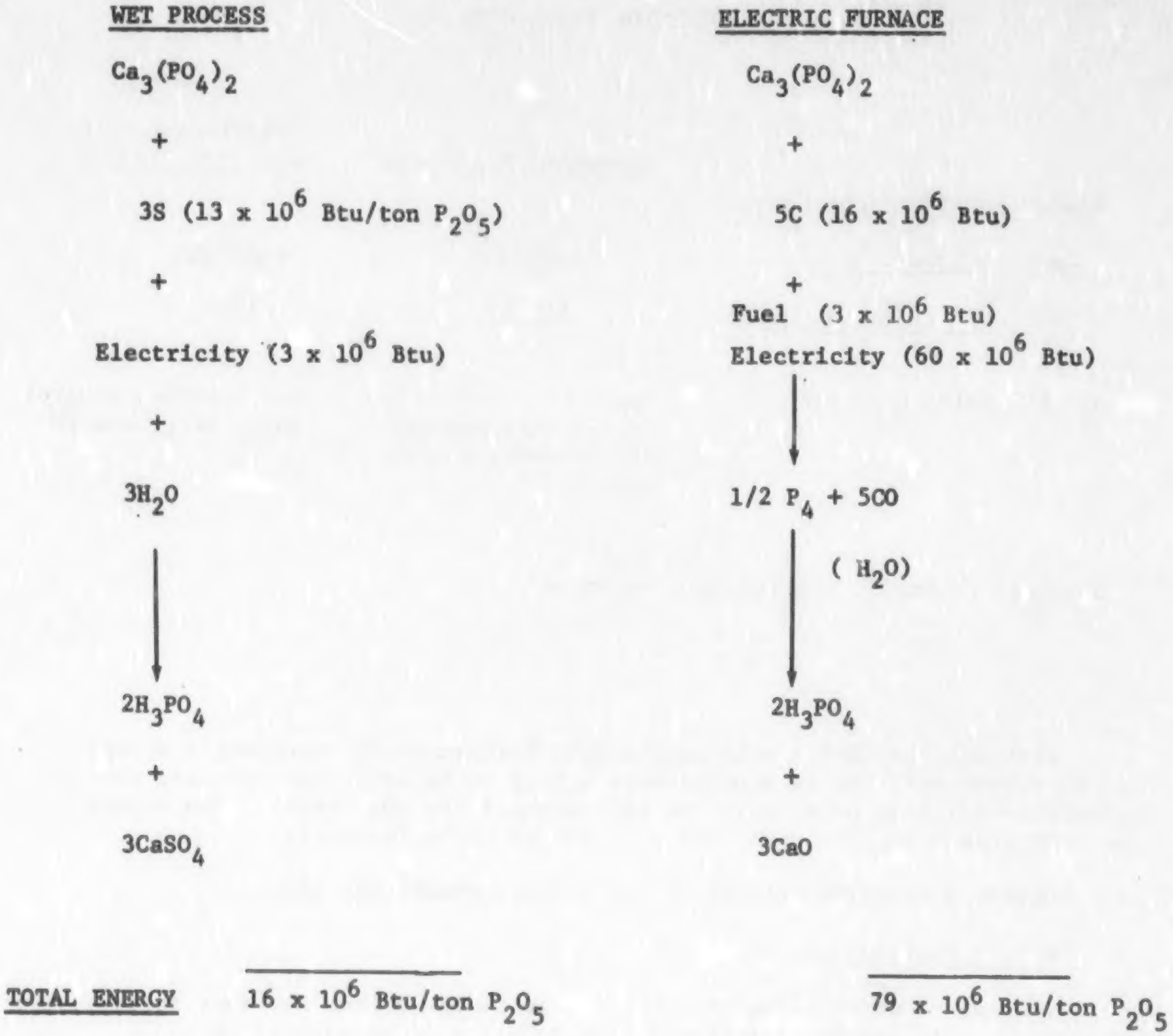
The cost also includes conversion of the P_2O_5 to the sodium salts in the proper stoichiometric mixture for STPP. The capital and operating costs for such a step should really be added to the cost of electrothermal acid to make the economics directly comparable.

A major uncertainty with either process is the escalating cost of energy, particularly electricity. We believe that this threat, plus the fact that large increments of investment at high risk are necessary for electric furnace phosphorus, will cause producers to consider seriously the cleanup of wet-process acid as a viable alternate for necessary expansion of supplies of detergent-grade phosphate.

Figure V-2 shows the overall energy consideration in the choice between the wet-process and electrothermal routes to clean phosphoric acid. It is assumed that the energy required for supplying phosphate rock is the same for each process, and that each method produces sodium phosphates in the proper ratio for STPP. The electrothermal route suffers from the major disadvantage that thermally expensive electric energy is expended to reduce phosphate rock to elemental phosphorus, but that the energy of reconversion to P_2O_5 is not recovered, but is lost as low-level heat in the phosphorus burner and acid plant. Another significant difference in the two methods, amounting to 3 x 10^6 Btu/ton of P_2O_5, is represented by the use of sulfur (13 x 10^6 Btu) as an overall chemical reagent in the wet process, as contrasted to carbon as fuel (16 x 10^6 Btu) in the electrothermal process. The electric furnace process was originally adopted to exploit cheap hydroelectric power, but today it must depend on thermal power. It inherently is penalized by the loss of almost 70% of the thermal energy in its fuel cycle producing electricity. This loss amounts to about 40 x 10^6 Btu/ton P_2O_5. Even without this penalty, however, 39 x 10^6 Btu/ton P_2O_5 are required at the electric furnace, and the method consumes 23 x 10^6 Btu/ton P_2O_5 more than the wet-process system.

On a total energy basis, the wet-process system can be operated at a fraction of the total energy required for the electrothermal process, and this saving is in electric energy where conservation is most urgently required.

The trade-offs to be considered from a pollution standpoint in choosing between the two methods are illustrated in Table V-6. Because a substantial amount of energy is saved as electrical energy, the equivalent pollution as stack effluent associated with that energy production is saved. From a process standpoint, we would be building a new wet-process unit and the required sulfuric acid unit to support production of 50,000 tpy of P_2O_5. It would be necessary to establish the necessary cooling pond and settling basins to accommodate the sludge, gypsum, and scrubber effluents from this system. The comparable units for a western electrothermal system would be larger, more expensive, and more difficult to operate. Rainfall is highly variable in the Mountain States, and problems of flash-flooding, and undependable water flow in small streams must be considered. Scrubbers would involve handling some very dusty materials such as carbon and silica, particularly from the phosphate nodulizing and handling systems. The electrothermal route also involves hazards with exposure to vent streams from the phosphorus furnace and to the notorious problems with "phossy" water which are not present in the wet-process sytems.


WET PROCESS
ELECTRIC FURNACE
$Ca_3(PO_4)_2$
+
3S (13×10^6 Btu/ton P_2O_5)
+
Electricity (3×10^6 Btu)
+
$3H_2O$
$2H_3PO_4$
+
$3CaSO_4$
$Ca_3(PO_4)_2$
+
5C (16×10^6 Btu)
+
Fuel (3×10^6 Btu)
Electricity (60×10^6 Btu)
1/2 P_4 + 5CO
(H_2O)
$2H_3PO_4$
+
3CaO
TOTAL ENERGY
16×10^6 Btu/ton P_2O_5
79×10^6 Btu/ton P_2O_5

Source: Arthur D. Little, Inc. estimates.

Figure V-2. Energy Comparison for Wet-Process and Electric Furnace Methods of Cleaning Phosphoric Acid

TABLE V-6

POLLUTION TRADE-OFFS

	Elemental Phosphorus	Wet-Process with Chemical Cleanup
Wastewater Treatment Costs		
Capital Investment	\$930,000	\$292,000
Unit Cost (\$/ton P_2O_5)	\$12.03	\$8.27
Air Pollution Control	Same, but dust loading is much heavier and includes carbon dust	Wet scrubber control dust, SiF_4, and HF

Source: Arthur D. Little, Inc. estimates.

Although the choice will be strongly influenced by a company's access to phosphate rock and economical electricity we believe that economic considerations influence adoption of the chemical cleanup option. The effect on both energy and the environment is likely to be favorable.

C. SOLVENT EXTRACTION CLEANUP OF WET-PROCESS PHOSPHORIC ACID

1. Process Description

Cleanup of wet-process phosphoric acid is based upon the fact that phosphoric acid can be transferred from solution in an aqueous phase to solution in an organic phase, such as normal butanol, and leave behind undesirable impurities, such as calcium chloride, in the aqueous layer. The organic phase can then be contacted in a separate unit with fresh water to yield a pure solution of phosphoric acid.

The process is illustrated in greatly simplified form in Figure V-3. After digestion of the phosphate rock, phosphoric acid extraction is achieved in countercurrent vertical columns. In the first of these, the calcium chloride brine containing crude phosphoric acid is pumped to the top of the column, and the waste brine is discharged from the bottom. The recirculated solvent stream, which has been stripped of phosphoric acid, is fed to the bottom of the column and flows out of the top after having

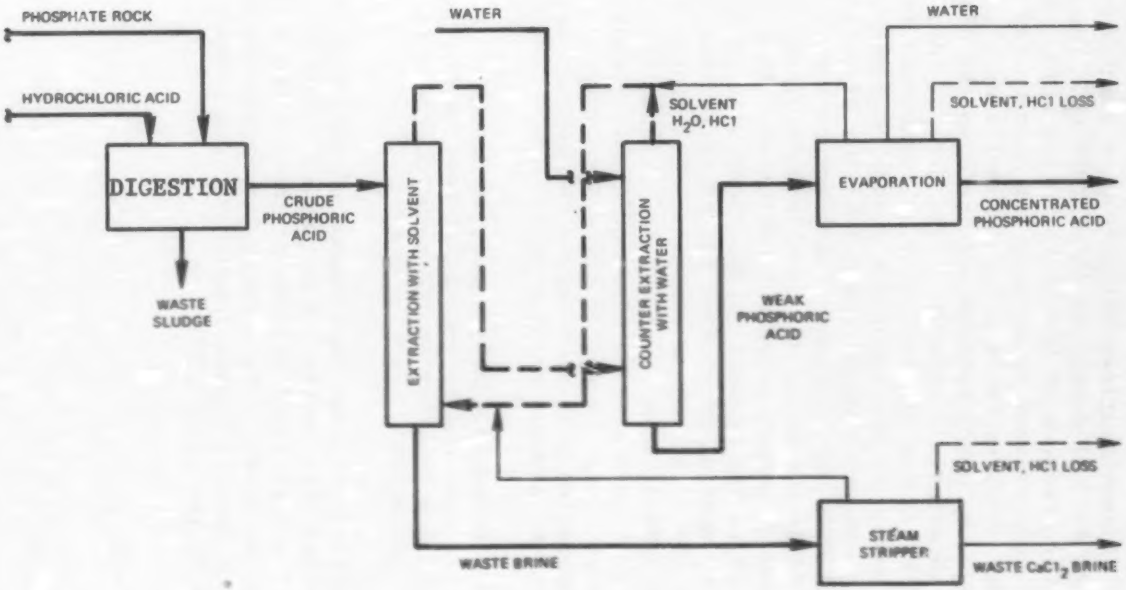

PHOSPHATE ROCK
HYDROCHLORIC ACID
DIGESTION
WASTE SLUDGE
CRUDE PHOSPHORIC ACID
EXTRACTION WITH SOLVENT
WATER
COUNTER EXTRACTION WITH WATER
SOLVENT H_2O, HC1
WEAK PHOSPHORIC ACID
EVAPORATION
WATER
SOLVENT, HC1 LOSS
CONCENTRATED PHOSPHORIC ACID
WASTE BRINE
STEAM STRIPPER
SOLVENT, HC1 LOSS
WASTE $CaC1_2$ BRINE

Figure V-3. Solvent Extraction Process for Phosphoric Acid - The IMI Process

extracted the phosphoric acid from the crude aqueous stream. Recovery of phosphate from the brine can be practiced at any degree desired if a sufficently large extraction unit is employed. The phosphate-carrying solvent stream is next contacted in the second extraction column. Fresh water is used as the stripping agent. The aqueous phase is the product acid, and the organic phase is recycled as solvent to the first extraction column.

There are a number of complications which require special handling; these are not illustrated in full detail on the flowsheet. The first of these complications is the presence of HCl in the crude acid. Although a wet-process system employing solvent extraction for cleanup may be practiced in the conventional manner with sulfuric acid, (Wasselle et al., 1966), there are a number of advantages in using hydrochloric acid as the digestion medium. One important advantage is economic. The process permits the use of waste HCl instead of requiring generation of sulfuric acid from sulfur. The calcium chloride produced in the digestion system improves the efficiency of the extraction system, reduces the solubility of solvent in the aqueous phase, and simplifies the problems of solvent recovery. The crude acid contains an appreciable excess of HCl to eliminate or reduce the concentration of monocalcium phosphate present in solution. This salt [$Ca(H_2PO_4)_2$] is extracted to the organic phase, along with phosphoric acid, and must be eliminated by special provisions in the extraction circuit. The solvent stream from the first column contains hydrochloric acid, extracted along with phosphoric acid. The HCl is stripped from the solvent and appears as part of the clean aqueous phosphoric acid stream. Unlike the calcium salt, however, it can be boiled off during evaporation of the product acid. This evaporation step also serves to separate and recover any solvent dissolved in the aqueous product acid.

The calcium chloride brine initially separated from the extraction step also contains hydrochloric acid and solvent which must be recovered. This recovery is accomplished in a steam-stripping step and the acid and solvent are recycled to the solvent stream.

There are many opportunities for improvement of this system through the development of solvents with better extraction efficiency, and through the use of both chemical and physical methods to improve the separation of the pure phosphoric acid at lower cost. Credit for aggressive development of this system belongs to Israeli Mining Industries, Ltd., which first demonstrated the method in the early 1960's.*

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*A recent paper presented to the Fertilizer Society of London in November of 1975 discusses some of the newer technology and the opportunities for its commercial exploitation. The reader is advised to consult this paper and Wasselle et al. for further details of the process.

2. Current Status

A demonstration unit with a 1 tpd of P_2O_5 capacity was established at Haifa in 1961 (Baniel et al., 1962). On the basis of this design, a 7-tpd unit was installed by Toyo Soda Manufacturing Company, Ltd., in Japan ("Hydrochloric-Based Route ...," 1962), and started up in 1962. About 1965, a similar unit was installed by FFM in Mexico.

In the United States, the Kaiser Aluminum and Chemical Company announced in 1962 its intention to build a $2,000,000 unit at Gramercy, Louisiana. Kaiser abandoned plans for this unit after design studies.* In 1963, Dow Chemical Company of Canada announced plans for a pilot plant at Sarnia, Ontario ("Dow to Test ...," 1963). The unit was stated to have a capacity of 35 tpd and was scheduled to start operating in 1965. Again, no public announcement has been made of the outcome of the project.

Both the Kaiser and the Dow efforts were aimed at exploiting the potential outlet for waste hydrochloric acid. It is likely that detailed design studies revealed that the system was quite a bit more complex than initially believed and the investment correspondingly high. Another possible economic problem lies in the need to keep solvent losses at a very low level. On a theoretical basis, there is no inherent loss of solvent, but the recirculation rate and the opportunity for inadvertent loss is high. Severe corrosion problems can be expected in this environment which include hydrochloric acid, phosphoric acid, calcium chloride, and wet solvent.

3. Effluents

On the basis of available information, it is difficult to make quantitative estimates of the pollution control problems associated with the solvent extraction process. The problems likely to be encountered are illustrated in qualitative fashion in Figure V-4. Most of the problems encountered in the sulfuric acid digestion system are also present in the hydrochloric acid-based solvent extraction system. Major differences include substitution of waste calcium chloride brine, instead of solid gypsum, the problem of acidic fumes compounded by the presence of hydrochloric acid, and the presence of solvent which adds a new dimension to the control of both aqueous and gaseous emissions.

Because of the high rate of reaction with hydrochloric acid and the volatility of this agent, it is desirable that the phosphate rock be calcined prior to digestion. This step is carried out in high-temperature rotary kilns. The operation is dusty. Large quantities of CO_2 are evolved if the rock contains much carbonate, and fluoride gases and particulate matter must be controlled.

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*("Hydrochloric-Based Route ...", 1962; Wasselle, et al., 1966)

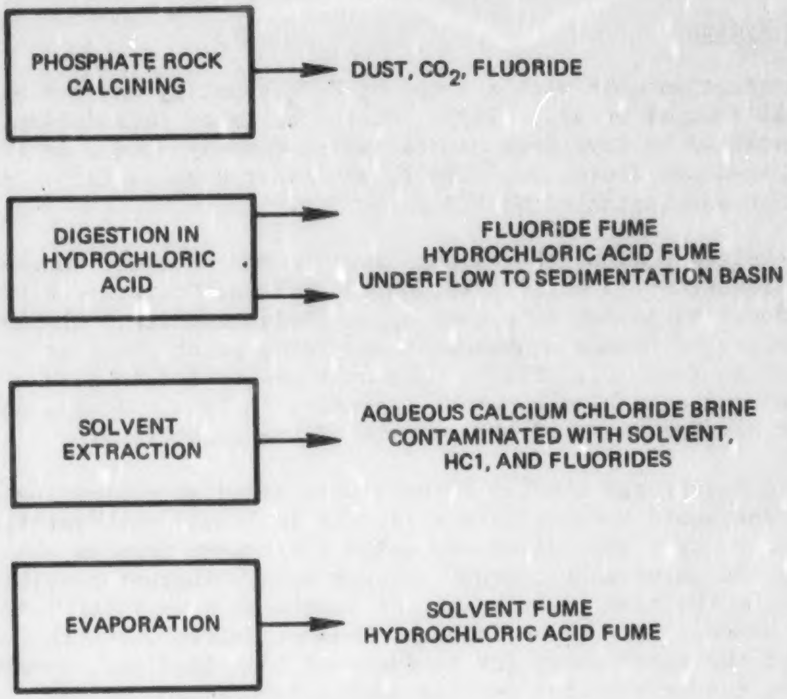
PHOSPHATE ROCK CALCINING
DUST, CO_2, FLUORIDE
DIGESTION IN HYDROCHLORIC ACID
FLUORIDE FUME
HYDROCHLORIC ACID FUME
UNDERFLOW TO SEDIMENTATION BASIN
SOLVENT EXTRACTION
AQUEOUS CALCIUM CHLORIDE BRINE CONTAMINATED WITH SOLVENT, HC1, AND FLUORIDES
EVAPORATION
SOLVENT FUME
HYDROCHLORIC ACID FUME

Figure V-4. Emission Problems Found in Solvent Extraction Process for Wet-Process Phosphoric Acid Cleanup

In the digestion step, the fluoride in the rock will be liberated as HF and SiF_4 vapor in the same manner as with digestion in sulfuric acid. The heat of reaction is considerably less than with sulfuric acid, but evaporative cooling is still required to control the temperature.

The major waste stream from the solvent extraction system is the calcium chloride brine after it has been stripped of phosphoric acid. HCl and solvent are vaporized from this brine before it is discharged. This operation is likely to produce an acid fume. The product acid is concentrated in an evaporator. Solvent vapors and hydrochloric acid vapors from the evaporator are condensed and recycled. Careful control of all vent streams from these operations is necessary to avoid losses of the volatile solvent and HCl.

a. Water Pollution

As in the case of the sulfuric acid-based, wet-process phosphoric acid process, undissolved inorganic solids separated from the digestor liquor must be impounded in large ponds. Because of the high solubility of calcium chloride and the general absence of sulfates, the volume of solids will be less than that of the sulfuric acid process, as there will be no calcium sulfate (gypsum) precipitate. The pond will therefore be somewhat smaller. As in the case of the base line sulfuric acid wet-process, overflow and pond water seepage must be controlled.

Phosphates and fluorides can be removed from the overflow water by means of lime treatment, as described under the base line wet-process in Chapter IV.

By far, the most significant wastewater stream from this process is the highly concentrated calcium chloride brine from the solvent extraction step. This stream also contains significant amounts of the n-butanol solvent. As can be seen from the estimated wastewater characteristics presented in Table V-7, the quantity of calcium chloride generated is very large - amounting to approximately 1.65 tons per ton of phosphorus. The problems that would be encountered with disposal of this brine are analogous to those encountered from soda ash plants using the Solvay process. These disposal problems have accelerated the closing of a number of U.S. Solvay plants, except where located on streams with large flows. If disposal of large amounts of calcium chloride brines into streams is prohibited, an assumption we believe is necessary for a plant of economic size, the only remaining disposal methods are:

1. Ocean dumping,
2. Deep-well disposal,
3. Evaporation to produce calcium chloride for sale, and
4. Solar evaporation.

The problems with each of these disposal methods are discussed below:

1. Ocean disposal of wastes is being discouraged as an official U.S. policy. Although these waste brines might be proven to have little ecological hazard when ocean-dumped, the costs of transport to an approved ocean-dumping site would probably be prohibitively expensive for plants located any distance from the ocean. For ocean disposal from plants located on the sea coasts, we estimate that the disposal costs for these brines would be in the range of $5 to $20/ton of phosphorous.

2. It appears that deep-well disposal of this brine would probably not be permitted, except at sites where unique geological conditions (an extensive saline aquifier) exist. While we have considerable doubts that approval would be given for deep-well disposal, we have chosen this method for developing pollution control cost estimates.

3. The production of $CaCl_2$ for sale would have to compete with $CaCl_2$ from Solvay Na_2CO_3 plants and this market is already limited - one of its largest uses being as a deicing chemical. We do not believe that the $CaCl_2$ product could compete with $CaCl_2$ that comes from present sources.

TABLE V-7

WET-PROCESS PRODUCTION OF PHOSPHORIC ACID WITH SOLVENT EXTRACTION PURIFICATION WASTEWATER CHARACTERISTICS

Wastewater Characteristic	Treated Pond Water Overflow		Solvent Extraction Brine		Total Wastewater Stream	
	(mg/l	(lb/day)	(mg/l)	(lb/day)	(mg/l)	(lb/day)
Total suspended solids	20	36	20	96	20	132
Phosphorus (P_4)	-	-	-	-	-	-
Phosphate (PO_4^{-3})	20	36	-	-	5.4	36
Sulfate (SO_4^{-2})	-	-	-	-	-	-
Fluoride (F^-)	15	27	-	-	4.1	27
Calcium chloride ($CaCl_2$)	100,000*	180,300	150,000	721,000	136,400	901,300
n - Butanol	-	-	250	1,200	180	1,200
Total acidity (as$CaCO_3$)	No data	No data	No data	No data	No data	No data
Wastewater Flowrate	0.216 mgd		0.576 mgd		0.792 mgd	

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* It is assumed that the pond liquor will contain 10% $CaCl_2$. The actual concentration will depend on the HCl concentration used in the digestion step.

Source: Arthur D. Little, Inc. estimates.

4. Solar evaporation would only be possible in extremely arid regions, and even there the $CaCl_2$ concentration would only rise to about 35 to 40 percent because of the stability of the hydrates. At these concentrations, the concentrated lagoons would represent a latent hazard should a violent rainfall wash out supporting dikes. Therefore, no estimates of costs were prepared for this mode of disposal.

As mentioned earlier, the treatment system chosen for cost estimation is envisioned to consist of:

1. Pond water-seepage control,

2. Lime treatment of pond water overflow to remove phosphates and fluorides, and

3. Deep-well injection of the combined treated pond overflow water and calcium chloride brine.

Cost estimates for such a system are presented in Table V-8.

Sludge from the lime treatment step could be disposed of on-site by pumping it back into the impoundment pond. As in the base line wet process, this sludge will contain high concentrations of phosphates and fluorides.

In considering the water pollution problems associated with this process, it should be remembered that the actual volume of wastewater discharge depends on the overall water balance of the plant, which in turn depends on the specific process configuration and local climatic conditions. Moreover, deep-well injection has recently been viewed, in general, as an environmentally unacceptable disposal method, and the ability to use it depends heavily on the local geological conditions.

4. Energy Requirements

A major difference between the energy requirements of the solvent extraction system and those of the conventional sulfuric acid wet-process plant is that in the former steam requirements are much higher and by-product steam is not available from acid manufacture. Clean acid produced by the extraction section is at about 15% phosphoric acid concentration. It must be evaporated to a concentration of about 60% P_2O_5. This evaporation requirement amounts to about 5 lb of water evaporated per lb of P_2O_5 produced. In the sulfuric acid route, concentration from 32% P_2O_5 to 54% product requires only 1.3 lb of water evaporation per lb of P_2O_5. The use of a multiple effect evaporator will help to minimize the steam requirement associated with this evaporation load, but an energy supply of about 10×10^6 Btu/ton of P_2O_5 product will still be required. Electricity requirements will be about 300 kWh/ton of P_2O_5, a little higher than for the conventional sulfur-based process.

TABLE V-8

WET-PROCESS PHOSPHORIC ACID PLUS SOLVENT EXTRACTION PURIFICATION WASTEWATER TREATMENT COSTS
(Basis: 50,000 tpy P_2O_5)

CAPITAL INVESTMENT	$636,000
DIRECT OPERATING COST	
Labor	110,400
Maintenance (labor and materials)	25,400
Chemicals	87,800
Electricity (@ $0.020/kWh)	81,000
Sludge disposal	91,000
TOTAL DIRECT OPERATING COST	$395,600
INDIRECT COSTS	
Depreciation (@ 9%)	57,200
Return on investment (@ 20%)	127,200
Taxes and insurance (@ 2%)	12,700
TOTAL INDIRECT COST	$197,100
TOTAL ANNUAL COST	$592,700
UNIT COST ($/ton as P_2O_5)	$ 11.85

Notes: 1. Treatment consists of:

a. Solid pond seepage control
b. Lime treatment of pond water overflow
c. Deep well injection of combined treated pond water overflow and solvent extraction brine.

2. Capital investment adjusted to March 1975 level (ENR=2126)

3, Quantities:

- Labor - 8975 man-hr/yr @ $12.30/hr (with OHD)
- Chemicals - 2700 tpy hydrated lime @ $32.50/ton
- Electricity - 4,047,000 kWh/yr @ $0.020/kWh
- Sludge - 45,500 tpy (wet basis) (sludge disposal on-site @ $2.00/wet ton)

Source: Arthur D. Little, Inc., estimates.

5. Economics

The cost of production of clean phosphoric acid by the IMI process at a rate of 50,000 tpy of P_2O_5 is detailed in Table V-9. Capital investment is estimated at $7,400,000 for construction of a plant in 1975. This figure is based on a study published by Kaiser and IMI in 1966 (Wasselle, et al., 1966). A minor modification has been made in the substitution of calcined rock to permit elimination of the carbon decolorization step. Kaiser's 1966 estimates for battery limits and offsite facilities amounted to $3,500,000; updating this figure to the 1975 basis brings it to $5,900,000. Sludge ponds and scrubbers and other pollution control devices not included as part of the wastewater system would require an additional $1,500,000, bringing the total to $7,400,000. Depreciation at an 11-year plant life and local taxes and insurance at 2% of capital investment per year contribute more than $16/ton to the cost of product.

Phosphate rock and hydrochloric acid are the raw materials required for the system. A high grade of dry, ground, calcined phosphate rock at 34% P_2O_5 is charged at a price of $35/ton. Our cost estimate is based upon an overall recovery of 95% of the P_2O_5 in this rock. This efficiency is less than that claimed in IMI and Kaiser studies, but commercial experience with the method is limited and opportunities for loss of phosphate are high. (The loss could be soluble P_2O_5, adding to the effluent problem.) Rock costs amount to about $108/ton of P_2O_5 product. The hydrochloric acid requirement at 2.1 tons per ton of P_2O_5 is about 20% in excess of the theoretical requirement for reaction with the apatite in the rock. Some of this acid is required for reaction with acid-consuming constituents of the ore other than apatite, but a large part of it represents physical losses from the system.

The price of acid at $30/ton represents a reasonable transfer value for this material, but the charge is arbitrary. The system is only economically practical when byproduct hydrochloric acid is available, and a fair charge for the acid depends upon alternative uses for it at the site of its production, or on the costs of its disposal. At $30/ton, the cost is equivalent to $63/ton of product, and is considerably more expensive than the sulfur cost for the conventional process. Hydrochloric acid would have to be priced at $18/ton to make its cost equivalent to that of sulfur at $45/ton.

The solvent makeup requirements are estimated at 8 lb/ton of product; a rate which is equivalent to the loss of about 50 lb/hr of solvent. The resulting charge to product is about $2/ton of P_2O_5. Inadequate control of potential points of solvent loss could result in losses much higher than this figure, and would overload the pollution control system.

TABLE V-9

ESTIMATED COST OF PHOSPHORIC ACID MANUFACTURE SOLVENT EXTRACTION CLEANUP - IMI PROCESS

Location: Midwest

Fixed Investment: $7,400,000

Annual/Design Capacity: 50,000 ton P_2O_5

Annual Production: 50,000 ton P_2O_5

	Units	Price $/Unit	Requirement Units/ton P_2O_5	Cost $/ton P_2O_5
VARIABLE COSTS				
Raw Materials & Reagent				
Phosphate Rock (34% P_2O_5)	tons	35.00	3.1	108.50
HCl (100% Basis)	tons	30.00	2.0	63.00
Solvent	lb	0.25	8	2.00
Energy				
Electricity	kWh	0.020	300	6.00
Steam	10^3 lb	1.00	10	10.00
Water	10^3 gal	0.03	45	1.35
Labor				
Direct Operating Labor	man-yr	15,000	8×10^{-4}	12.00
Direct Supervision	man-yr	20,000	1×10^{-4}	2.00
Maintenance Labor	4% of CI			5.92
Maintenance Material	4% of CI			5.92
Labor Overhead	30% Labor			5.98
TOTAL VARIABLE COST				222.67
FIXED COST				
Plant Overhead	70% Labor			13.94
Local Taxes & Ins.	2% of CI			2.96
Depreciation	9% of CI			13.32
TOTAL COST OF MANUFACTURE				252.89

Source: Arthur D. Little, Inc., estimates.

Requirements for electricity and steam have been discussed above. The resulting charges total about $16/ton of product. The labor costs of about $14/ton are based on an operating staff of 40 men; maintenance requirements are estimated at about 8% of capital investment per year and are equally divided between maintenance labor and maintenance material. Total cost is about $12/ton of product. The total annual maintenance bill is about $600,000 per year. This figure is not unduly pessimistic in view of the extremely corrosive nature of the acidic process streams.

Total cost of manufacture of clean phosphoric acid by this method is indicated to be about $253 per ton of P_2O_5.

6. Assessment

At $253/ton of P_2O_5, clean phosphoric acid by the solvent extraction process would be competitive with the chemical cleanup system and not much different from the cost of acid derived from elemental phosphorus. The likelihood of achieving these economies requires several favorable circumstances. Most important is that the producer must have access to a source of byproduct hydrochloric acid at $30/ton or less. The plant will be located at the place where the acid is available and costs for disposing of the byproduct calcium chloride must be manageable. This probably means that deep-well injection has to be permitted, or that the plant site must be adjacent to a major waterway, so that direct disposal of the neutralized brine is permissible. Under these circumstances the adoption of this method would probably be acceptable from an environmental standpoint, because problems of disposal of the calcium chloride brine replace equally difficult pollution problems with byproduct hydrochloric acid.

An unknown factor, however, is the severity of the solvent control problem. At the solvent loss rate claimed (50 lb/hr of butanol) control costs are not severe. Failure to achieve this solvent efficiency, however, in addition to being a severe economic penalty could result in unmanageable BOD problems.

From the point of view of plant operations, this system must be classed as very difficult. Hydrochloric acid by itself is one of the more corrosive chemicals. When mixed with saline solutions and with phosphoric acid, and with the added complication of the acidic mixed aqueous and organic phases, the potential for extreme corrosion exists.

In view of these process uncertainties, there appears to be less likelihood that this option will be chosen than will the chemical cleanup method as an alternative to expanded electrothermal production. It would probably require an integration with a byproduct HCl disposal problem.

D. THE USE OF BYPRODUCT SULFURIC ACID

A conventional wet-process plant for phosphoric acid consists of two distinct process units. In the first, sulfur is converted to sulfuric acid; in the second, sulfuric acid is used as a reagent to convert phosphate rock to phosphoric acid. Byproduct steam from the sulfuric acid unit is used to advantage in the phosphoric acid unit, principally for the evaporation of dilute phosphoric acid from the filtration system. Sulfur is a major element of the production cost of phosphoric acid amounting to about \$38/ton of P_2O_5. At the right price, the phosphoric acid producer would be tempted to use byproduct sulfuric acid in place of the sulfur.

One site where favorable circumstances might exist is at Tampa, Florida, where there is a large electric utility. Tampa is also the principal transit point for shipment of phosphate rock from the Florida fields, and is already the site of substantial phosphoric acid production. The Tampa Electric Company operates four generating units at a capacity of 400 MW each. It has been estimated that when operating on 3.5 percent sulfur coal, each of these units could produce 100×10^6 lb/yr of SO_2; this estimate was based upon a 60% load factor for the generator. The byproduct sulfuric acid from all four units would support a phosphoric acid production of only 112,000 tpy of P_2O_5, a rate which is very small in comparison to units now operating in Florida. Byproduct sulfuric acid can be considered only as a supplemental supply rather than a primary source of sulfur for the phosphoric acid plant. Even if the load factor were increased to 100%, the unit could not support a full size phosphoric acid plant.

Under these circumstances, it is likely that the utility would have to offer sulfuric acid at a price under \$20/ton to interest the phosphoric acid manufacturer to contract for its supply. Steam to replace that lost by captive manufacture of sulfuric acid would also have to be part of the commercial arrangement. The phosphoric acid producer would be reluctant to engage in a firm, long-term contract, because the potential profits do not appear to justify the risk of dependence on the utility for a reliable supply of acid. The phosphoric acid producer would probably elect to install sufficient sulfuric acid manufacturing capacity for his entire needs in the event that supply of the fraction from the utility were interrupted. Although realizing no savings on capital investment for his plant, the arrangement would save the energy associated with production of the equivalent sulfur and its shipment to the plant site and conversion to sulfuric acid. Associated polution problems would also be eliminated. These benefits are marginal, however, and we do not believe it would influence the decision in any material way.

E. STRONG PHOSPHORIC ACID PROCESSES

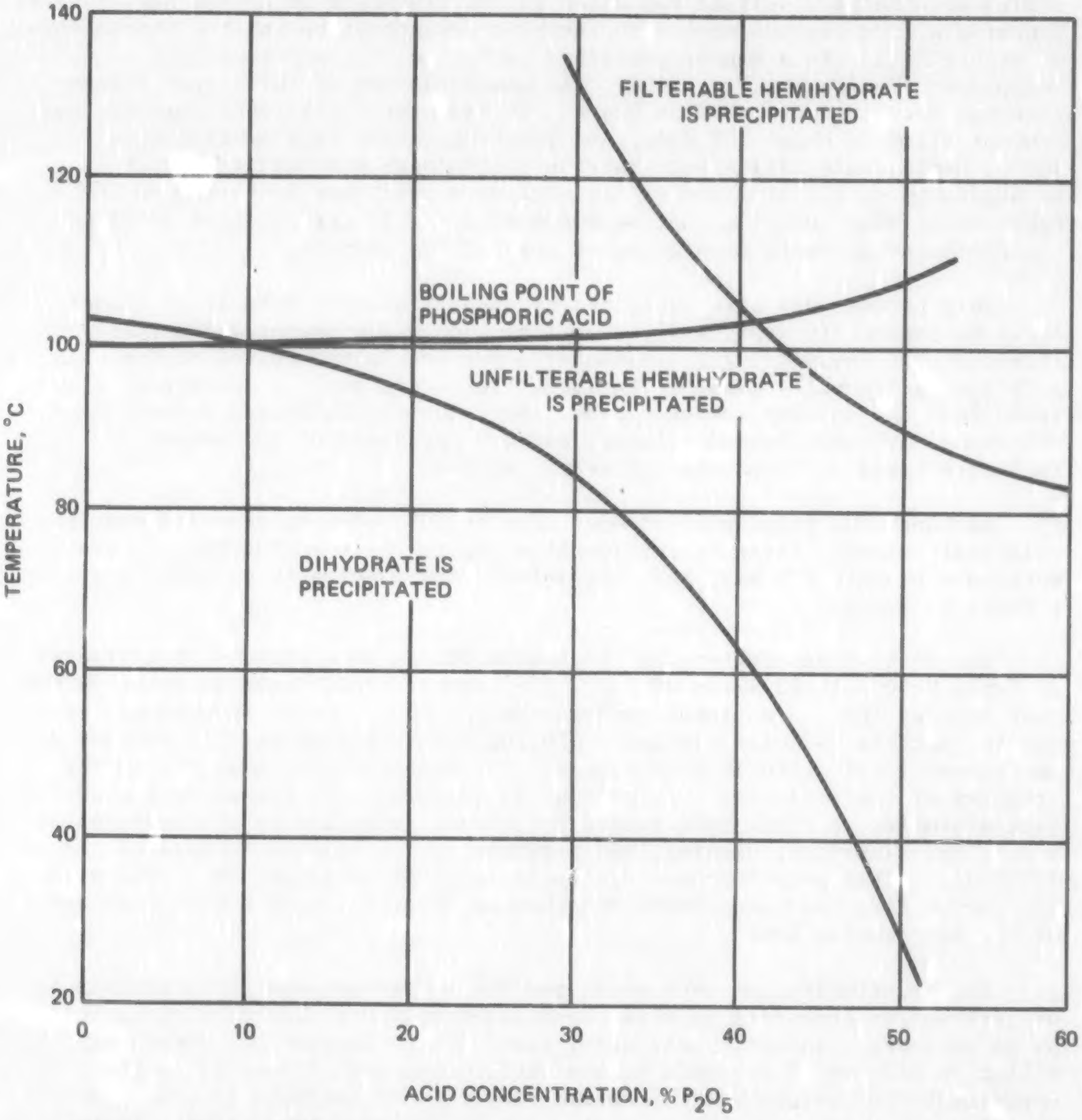
The success of a process for digestion of phosphate rock and sulfuric acid depends upon management of the step in which calcium sulfate is precipitated. Calcium sulfate can exist as the dihydrate or as the hemihydrate. The stable form depends upon both the acid concentration and the temperature of precipitation in a manner described in Figure V-5, attributed to Nordengren (Van Wazer, Jr., 1961). An understanding of this phase phenomenon has been the work of many years. It has been established that if the concentration is about 50% P_2O_5, and the temperature of digestion about 100°C, hemihydrate will precipitate in a form stable enough to permit it to be separated on a filter and washed without appreciable hydration to the dihydrate. This reaction must be avoided on the filter, because it blinds the cloth and prevents dewatering of the calcium sulfate.

This process has been exploited by several groups, notably by Fisons Ltd., in England (Crerar, 1973, Blumrich) and by Singmaster and Breyer (Singmaster & Breyer, 1973, Singmaster & Breyer) in the United States. In addition to its pilot plant in England, Fisons has built a commercial plant in Holland and another in Yugoslavia. Both the economics and process descriptions have also been disclosed, and our appraisal of the method is therefore based on these disclosures by Fisons.

Although the principles of operation at 50% P_2O_5, as stated above, are relatively simple, there is considerable expertise in making the process work on a practical basis, and this information is closely guarded by the process licensors.

The cost of manufacture by the Fisons strong acid process is estimated in Table V-10. At \$209/ton of P_2O_5, the cost of manufacture is about \$4/ton less than by the conventional wet-process method. Capital investment for the two methods is quite similar - \$10,100,000 by Fisons and \$10,200,000 by the conventional sulfuric acid system. The difference is well within the accuracy of the estimates. As originally proposed, the Fisons system was a little simpler, but the P_2O_5 recovery has been increased by the addition of a unit for slurrying, washing, and refiltering the calcium sulfate as the dihydrate. This step improves the yield from 96% to almost 99%. The added investment from this step about compensates for the saving and elimination of the evaporation step.

The opportunity for even small savings by the stronger acid process is of interest to companies in this competitive business, but as long as the plant includes a sulfuric acid unit, there are no appreciable energy or pollution effects of interest to our study. The method does offer the opportunity to operate with purchased sulfuric acid without incurring the penalty of having to purchase steam. But as outlined in paragraph D, no appreciable use of byproduct sulfuric acid can be expected in the industry.



Source: Van Wazer, p. 1049.

Figure V-5. Phase Diagram, $CaSO_4$ Precipitation

TABLE V-10

PHOSPHORIC ACID - FISONS STRONG ACID PROCESS

Location: Midwest

Annual/Design Capacity: 50,000 tons P_2O_5

Fixed Investment: $10,100,000

Annual Production: 50,000 tons P_2O_5

	Units	Price $/Unit	Units/ ton P_2O_5	Cost $/ton P_2O_5
VARIABLE COSTS				
Raw Materials & Chemicals				
Phosphate Rock	tons	30.00	3.40	102.00
Sulfur	tons	45.00	0.84	37.80
Energy				
Electricity	kWh	0.020	215	4.30
Water	10^3 gal	0.03	3.0	0.09
Labor				
Direct Operating Labor	man-yr	15,000	7×10^{-4}	10.50
Direct Supervision	man-yr	20,000	1×10^{-4}	2.00
Maintenance Labor	2% of CI			4.04
Maintenance Material	3% of CI			6.06
Labor Overhead,	30% Labor			5.57
TOTAL VARIABLE COST				172.36
FIXED COSTS				
Plant Overhead	70% Labor			13.04
Local Taxes & Ins.	2% of CI			4.04
Depreciation	9% of CI			18.18
TOTAL COST OF MANUFACTURE				207.62
RETURN ON INVESTMENT (Pretax)				40.40
POLLUTION CONTROL				6.86
TOTAL				254.88

Source: Arthur D. Little, Inc., estimates.

F. SECONDARY OPTIONS

1. Variations of Basic Wet-Process Technology

Modern processes for production of phosphoric acid by a reaction of phosphate rock with sulfuric acid are the result of many years of invention and improvement. This work has involved all three major steps: digestion, filtration, and evaporation. Both process conditions and processing machinery have been refined to a high state of efficiency and economy. A number of operating and construction companies own these processes, and most of them are available for license. Each has its proponents, but within the scope of this study we believe differences among them are not important in assessing pollution control problems, energy efficiency, or process economics.

2. Blast-Furnace Phosphorus

The essential requirements of the process for reduction of phosphate rock to elemental phosphorus are to supply the energy required for the endothermic reaction and to supply an acceptor for the oxygen released. The electric furnace supplies the energy by passing an electric current through the charge. The same result (Waggaman, 1961, Waggaman, 1950) can be achieved by supplying heat from gas blown through the furnace from the bottom, as in blast-furnace production of pig iron. In addition to the coke required for reaction with the phosphate rock, coke must be burned with air at about 130 x 10^6 Btu/ton phosphorus.

The result is a furnace much larger, more complex, and more costly than the electric furnace. It operates at a gas volumetric rate about seven times that of the electric furnace.

Despite these handicaps, a few blast furnaces were built and operated commercially in the days before TVA made electricity cheap and abundant near the phosphate fields. It is not likely that the demand for elemental phosphorus and shortage of electricity will again make the blast furnace attractive, but industry analysts should be aware of the availability of the process. A comparison of significant factors is tabulated below:

	Electric Furnace	Blast Furnace
Investment factor	1.0	1.6
P_4 efficiency	92%	88%
Coke, tons/ton P_4	1.9	5.5
Heat recovery factor	1.0	0.7
Furnace gas volume factor	1	7

Pollution control problems would be magnified as a function of the much higher volume of hot furnace gas. In view of the severe economic disadvantage implied by this comparison, we believe it unlikely that interest in blast furnace phosphorus will be revived.

3. Uranium Extraction

There is a small amount of uranium in phosphate rock, and it is dissolved as part of the 32% acid in the wet-process system. In the 1950's there were three plants where solvent extraction units were operated commercially to supply this uranium to the AEC. All were plagued with operating difficulties, both in the uranium plant and in its effect on the phosphoric acid plant. None was economically successful and all were shut down in favor of more conventional methods of uranium processing.

There is a current revival of interest in this source of uranium (Ross, 1975); several development programs are underway and one plant is under construction. The processes have been refined on the basis of new solvent systems and will be watched with interest. The scale of phosphate rock processing is such that it represents a substantial uranium resource. Problems of pollution control are substantial and are similar to those encountered in the solvent extraction process for cleanup of wet-process acid. The EPA should perhaps monitor this development, and perhaps, at an appropriate time, assist in solving these problems.

4. Exploitation of Low-Grade Phosphate Reserves

There are two sources of phosphate which are not currently being exploited. One is in strata which are left in the ground in favor of richer material; the second consists of phosphate slimes produced as tailings from beneficiation. Consideration of exploitation of these reserves is outside the scope of this study by the specific exclusion of mining and milling processes, but their importance at least demands mention.

Mining of low-grade material, either underground hard rock in the West or Florida overburden now rejected, will be necessary when the higher grades are exhausted. It will be more expensive, require more energy, and produce more waste than the current system.

Recovery of phosphate from tailings of current operations may come about if the technology can be developed. But it has been a research effort for many years without real success. Operating costs and energy requirements would be high, but phosphate-free tailing would be more ecologically acceptable.

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